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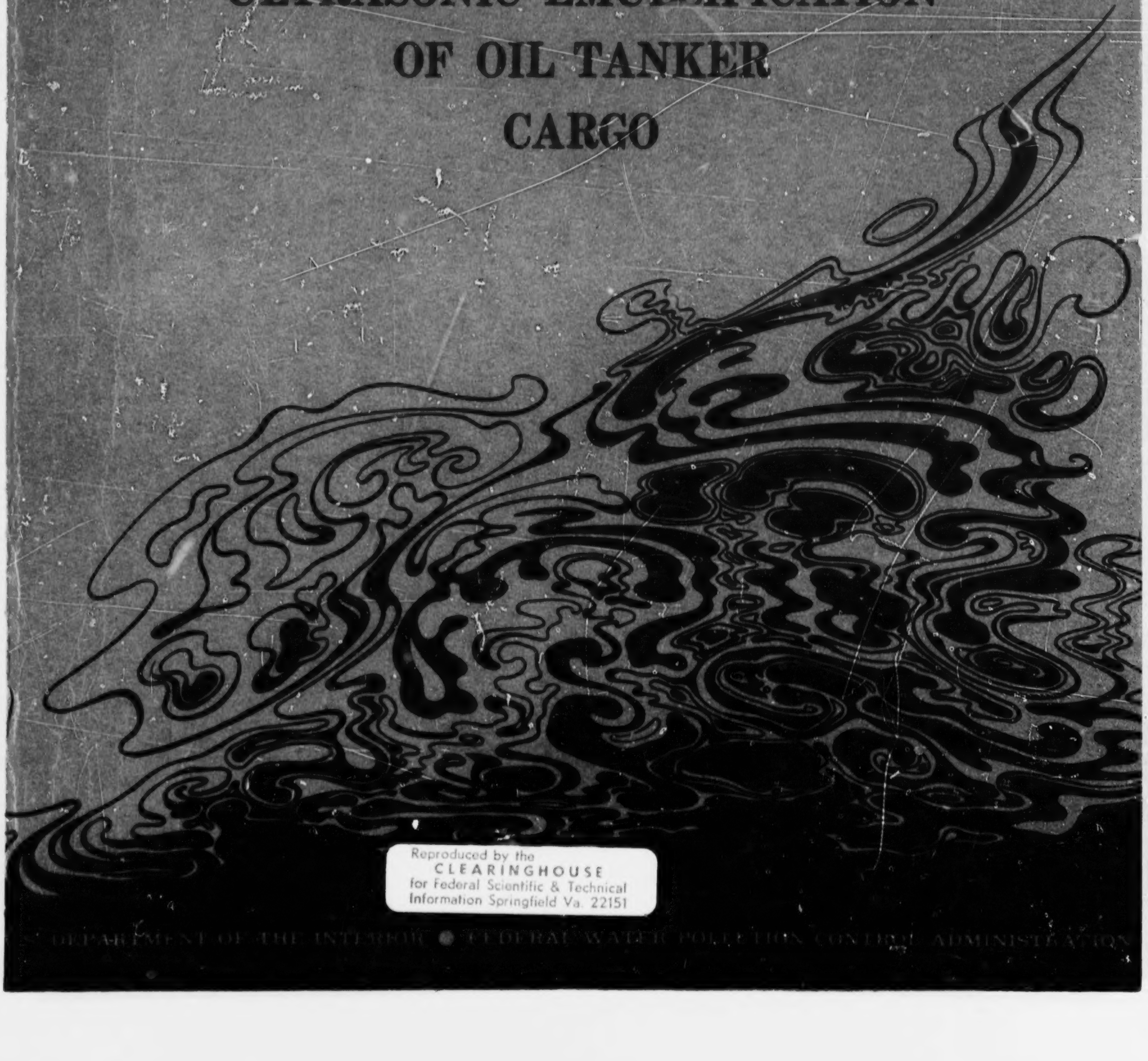
ULTRASONIC EMULSIFICATION OF OIL TANKER CARGO



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S. DEPARTMENT OF THE INTERIOR • FEDERAL WATER POLLUTION CONTROL ADMINISTRATION

ULTRASONIC EMULSIFICATION OF OIL TANKER CARGO

Feasibility Study Using an Ultrasonic Process to Emulsify Petroleum to Reduce Oil Slick Hazards in Event of Spillage at Sea

FEDERAL WATER POLLUTION CONTROL ADMINISTRATION
DEPARTMENT OF THE INTERIOR

by

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Program No.
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FWPCA Review Notice

This report has been reviewed by the Federal Water Pollution Control Administration and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Federal Water Pollution Control Administration.

ABSTRACT

As a pollution preventive concept, the ultrasonic emulsification of oil for marine transportation has been tested for feasibility. Two crude oils and a common fuel oil were emulsified and tested. The emulsions are characterized as stable, dispersible in sea water, not unduly toxic and with reduced fire hazard potentials. This laboratory study shows that oil emulsions can be created by ultrasonics in a continuous process at tanker loading rates. Limited economic evaluation shows the concept to be meritorious and reasonable.

PURPOSE OF PROJECT

The purpose of this project was to study the feasibility of producing emulsified oil at a rate comparable with conventional tanker loading rates and to investigate the economic and ecological factors.

SCOPE OF PROJECT

To determine blender design parameters and emulsified oil characteristics, two crude oils and one fuel oil were chosen. A Libyan light oil, a Venezuelan oil and #6 Fuel Oil were used.

Only two emulsifiers were used and they were base-neutralized sulfonated nonionics. These are compatible with sea water and of low toxicity.

The emulsions tested were oil-in-water. Oil was the internal phase and 97% of the total. Water and chemical was the external phase and 3% of the total. The tests on the emulsions were to determine: stability under simulated transportation conditions, dispersibility in sea water, toxicity to fish, and product alteration. Included were tests with safety aspects: evaporation rates, flash points, vapor pressures and rupture leak tests.

An economic study was made which shows emulsification costs of about 20 cents per barrel without considering possible offsets or side benefits.

This report was submitted in fulfillment of Contract 14-12-559 between the Federal Water Pollution Control Administration and Sonics International, Inc.

KEY WORDS

Continuous Process
Petroleum
Toxicity
Tanker
Water Pollution
Ultrasonics
Emulsion Stability
Safety
Transportation
Emulsification
Dispersion
Flammability
Spills

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1. CONCLUSIONS

This report covers the ultrasonic emulsification of oils for tanker transportation as a pollution preventive concept. Tests performed show that this is no longer just a concept, but with reasonable refinement, is a practical method. This oil spill preventive method is a fail-safe method because no decision is required when disaster impends.

Crude oils have been emulsified by a continuous flow-through process with 97% oil as the inner phase. The continuous and outer phase of the emulsion is 2.5% water and 0.5% chemical emulsifiers. Briefly, the ultrasonic emulsification technique is as follows: (1) an emulsion seed is created by passing oil, water and emulsifier through an ultrasonic homogenizer, (2) the emulsion seed is 70% oil and 30% water (and emulsifier), (3) the seed (10%) is blended with raw oil (90%) for the final emulsion.

1.

Data from the laboratory emulsification unit show that full size units for tanker loadings are practical. A 100 barrel per minute module unit was designed for single or multi-unit applications. Skid base size is 10 ft. x 27 1/2 ft. with a 27 ft. 7 in. blending column at one end.

2.

A flat plate ultrasonic transducer was developed during the course of this study. This device has application in high rate, continuous, emulsification process.

3.

The emulsions studied are stable in a quiescent state at temperatures from 25° F to 140° F. Gentle agitation as provided by simulated ship motion improves emulsion stability.

4.

Emulsion dispersion tests, in sea water with one percent emulsions, show only trace amounts of free oil after twenty-four hours. We conclude that if an emulsion were spilled at sea, no oil slick would form. Test conditions were more exacting than those at sea. In reality, the emulsion would be spread out so far and become so diluted in only a few hours that before break-back could occur, oil droplets would be spread too far apart to form an oil slick.

5.

Our toxicity tests on fish determined that emulsions of heavy oils are less toxic than those of light oils. This is in line with published literature and data. Also, comparing emulsion toxicities with reported oil toxicities, in confined spaces, the emulsion is more toxic than the oil. This is believed to be due to the fact that the fish were in more intimate contact with the emulsion. It is reasonable to believe that emulsions released at sea will be dispersed by wind, tide and ocean currents and rapidly diluted below the toxic level.

The toxicity tests were static tests and not flow-through. The tests are discussed in detail elsewhere in the report.

6.

In an open system there was a tenfold reduction in evaporation rates due to emulsification. The evaporation rates for the three emulsions in a partially open system (vented) are the same as for non-emulsions. In a transportation or normal handling situation, emulsification does not reduce loss due to evaporation. However, in the case of a spill at sea, the tenfold reduction (open system) is of significance. This reduced rate would have a safety value in the immediate vicinity of a spill (reduced fire hazard).

7.

Emulsification significantly improves the safety of the transportation and handling of liquid hydrocarbons. Two things are changed: (1) fire hazard is reduced and (2) spill rate is reduced. The Zueitina crude had a flash point of 42°F and after emulsification it was raised to 84°F. The flash point of the Tia Juana crude was raised from 64°F to 96°F. In addition, the emulsified oil, due to the higher conductivity of the water, has a lowered static electrical charge potential. All these factors reduce the chance of fire and explosion and, due to the slower burning rate of emulsion, provide more time for control in case there is a fire. This reduced fire hazard could reduce insurance rates.

8.

The formation of tank bottoms and sediment build-up on the walls of compartments will be reduced or eliminated. Pollution of ocean environments by oil slicks resulting from tank cleaning or ballast discharge could virtually be eliminated.

9.

The chemical and physical character of the two crudes and the fuel oil tested were not altered by emulsification. About seventy-five percent of the water soluble salts contained in the oils were removed as a result of the emulsification and demulsification process. This upgrading could be a cost offset in the case of high salt content crudes.

10.

Means and cost to break emulsions as used in this study were based on work of others. Means to break-back are: (1) atomization, (2) chemicals, (3) pumps and (4) combinations of the foregoing.

11.

The study suggests that emulsified # 6 **Fuel Oil** can be used as ship fuel without break-back. This would be an improvement in safety due to less chance of fire in case of accident or other uncontrolled occurrences. Also there would be less tank cleaning required and thereby, a reduction in ocean pollution.

12.

Economic analyses indicate emulsification costs are about 20 cents per barrel without any consideration for demulsification or possible cost offsets. Modifications of the procedure itself hold potential for reductions in process costs.

2. RECOMMENDATIONS

Results of this feasibility study show that the ultrasonic emulsification concept for the transportation and handling of oil is reasonable. The mechanics of emulsification and the character of the emulsions have been well defined. Overall economics are not as well defined, but from data available, appear reasonable. For a complete and more realistic appraisal of the concept, two factors that require refinement are emulsifier costs and break-back costs. The study permitted the evaluation of only two emulsifiers and as a necessity they were selected strictly on performance. Break-back techniques were not within the scope of this study.

Results of tests performed on the emulsions strongly suggest use of emulsified oil as ship fuel. About the only thing required to finalize this concept would be some actual burner tests. Two of the advantages would be: safety and elimination of sediment in tanks. The reduction and/or elimination of fuel tank bottoms has one obvious pollution abatement aspect, the elimination of dumping. We recommend that action be taken on this concept with the proper Marine and Transportation Authorities.

During the course of this feasibility study a flat plate transducer was developed. This device has application in the ultrasonic emulsion seed process for oils. The disclosure was made in the second monthly progress report (9 September 1969). Patent proceedings should be initiated for the U.S. Government by the F.W.P.C.A.

In view of the results obtained in this study, we believe that justification exists for further investigations and refinements of economics. Listed are our recommendations for further definition of the concept.

1. Optimize emulsifiers as to concentrations and cost. Determine reuse characteristics.
2. Develop low cost break-back technique.
3. Evaluate economic offsets and safety features.
4. Evaluate desalting as a result of this complete process.
5. Evaluate emulsified fuel oil as a ship fuel.
6. Upgrade economics based on items 1 through 5.
7. Actual dispersion tests at sea after satisfactory completion of above items.

8. Toxicity tests on optimum emulsifiers and emulsions at the FWPCA Marine Laboratory. These tests, if needed, should be on a flow-through basis that takes into account continual dispersion.

9. Construction and demonstration of emulsification and demulsification unit. This should be after all other work is completed.

Some discussion of factors for investigation follows:

Optimize Emulsifiers

The chemical cost is the greatest single cost in this ultrasonic emulsification process. A reduction in this cost will greatly enhance the economics of the process. Additional investigations are needed to develop: (1) a group of low cost emulsifiers with reasonable stability (2) emulsifiers that can be used at minimum concentrations (less than 0.5%), (3) emulsifiers that can be reclaimed and reused (4) better overall economics.

Emulsion Break-Back

The emulsions studied were broken by chemical demulsifiers and no investigations were made of other techniques. The total economics can be greatly improved by the elimination of demulsifier chemicals. A low cost and practical break-back technique that is compatible with the rest of the concept is needed. Prior work by others indicates that emulsions can be broken mechanically. Shearing action can rupture the outer phase of emulsions and this is one of the reasons we believe that pumps should be studied.

The investigation should include evaluation of pumps, pumps with nozzels or jets, heat and restricted use of chemicals. Also, the use of ultrasonic equipment should be tested in combination with above as well as singly. Economics developed will apply to the total process or concept.

Economic and Safety Offsets

Certain features of the emulsification concept suggest other advantages. These features should be investigated to better define their values. Briefly these are: (1) tanker maintenance, including bottom sediments and corrosion, (2) safety due to electrostatic charge reduction, lowered flash points, reduced burn rates and reduced evaporation, (3) desalting of oils, and (4) use of emulsions as a ship fuel.

Desalting

This study has shown that some product up-grading is accomplished as an end result of the ultrasonic emulsification process. Water soluble materials were removed from the three oils tested. The reduction in water soluble materials was in the order of 75 to 90%.

The three oils tested were not high salt content oils. The Zueitina Crude contained about 28 pounds of water soluble salts/1000 bbls. of oil when received in our laboratory. After ultrasonic emulsification using 30 bbls. water/1000 bbls. oil in the process and subsequent chemical break-back the crude contained only 7 pounds of water solubles per 1000 bbls. of oil. This is an indicated reduction of about 75%. Thirty barrels of water can carry about 3000 pounds of salt in solution. Test results on the Tia Juana Crude and the #6 Fuel Oil were similar. As explanation, the fresh water used to make the emulsion is mixed very thoroughly with the oil during the emulsification process. The water dissolves salt crystals and also mixes with brine present in the oil. When the emulsion is broken back, the water contains the salt in solution. All these data indicate the high salt content crudes can be effectively desalted as a side benefit of this ultrasonic process.

We recommend that work be done to determine the desalting characteristics of the ultrasonic emulsified oil handling concept including disposition of the recovered brine. The disposal will depend on several things: (1) facilities at the terminal, (2) emulsifier content, and (3) reuse of water and emulsifier. It will not create a pollution problem. The investigation should be made on several crudes with high salt content. Also, an economic investigation should be made to determine the value of desalting process. This study will provide economic data to offset some of the costs of the ultrasonic process.

Dispersion Tests at Sea

We recommend that dispersion tests be performed at sea. Several spill tests of about one barrel each should be made with emulsified oils and with raw oils for comparisons. The data to be gathered would provide information for dispersion rates, emulsion or oil concentrations at various distances with respect to time and flammability of the spill at different time intervals. These tests should be made under varying sea conditions ranging from calm to high. At least one test should be made on a large lake to simulate a spill in a bay area. These tests must be made in a controlled area and after emulsifiers have been optimized.

3. INTRODUCTION

3.1 Problem Background

In recent years the threat of oil pollution of the waterways, seas and beaches has increased with the rapidly increasing volume of oil and oil products which is transported in barges and tankers. As the number of petroleum product laden vessels and the waterborne traffic increases there is increased danger of oil spillage due to collision, accidental grounding, or other breakage.

Compounding this danger of large scale oil spillage is the ever increasing size of tankers. In 1945 a world fleet of 1,911 tankers could carry 24 million tons of oil and oil products, and the largest supertanker was rated 23,000 deadweight tons. In 1956, the world's fleet had grown to 2,778 tankers with a total capacity of 45 million tons, and the largest supertanker had a capacity of 45,000 deadweight tons. By 1966 the number of tankers was 3,524, and their combined capacity was 103 million deadweight tons. The largest supertanker in 1966 had a capacity of 210,000 deadweight tons.[1] There are now many 210,000-deadweight-ton tankers,[2] several 312,000-deadweight-ton tankers in service or under construction and even larger ones (500,000 to 1,000,000 deadweight tons) are being planned.[3,4,5] Oil tankers account for about 40 percent of the worlds ocean going traffic, and carry about half of the worlds total ocean tonnage.

Barges are also increasing in size and number. With the rapid expansion of off-shore production, tank barges have grown larger than the average World War II tanker. Tank barges with a capacity of 20,000 tons are in operation and 30,000 ton barges are planned. In 1967 there were 2,781 tank barges with a net cargo capacity of 5,120,029 tons.[6]

In 1967 about 173 million tons of crude oil and petroleum products were transported on the 25,380 miles of inland waterways. Crude oil and petroleum products accounted for 35 percent of the total inland waterway tonnage. About 72 percent of the inland waterway tonnage is transported by barges.[6]

As more supertankers are being placed into service each year the probability of catastrophic oil spills is consequently increased. One of the most dramatic examples of such catastrophic oil spills is the grounding of the Torrey Canyon off the southwest coast of England on March 18, 1967. The Torrey Canyon was a 127,000-ton displacement tanker loaded with 118,000 tons (900,000 barrels) of Kuwait crude oil. About 13,000 tons of the oil spilled by the Torrey Canyon was washed onto the Cornish beaches.[7]

It is not possible to predict where or when the next major spill will occur. However, on the average, tankers will be involved in one major oil spill and more than 100 minor accidents per year. Since most of these accidents are results of human error, it will not be possible to completely eliminate tanker accidents. In addition to the oil spills resulting from tanker and barge accidents are the many unknown negligent spills resulting from handling errors, vessel leaks and illegal discharge of bilge washings. Estimates of the yearly addition of oil to the sea range from one million to 100 million tons.

Present technology does not make it possible to accurately predict the behavior of specific oil spills. However, studies of previous oil spills permit some generalizations about the behavioral characteristics of an oil slick. Upon making contact with the water an oil spill rapidly spreads in a constantly thinning layer. The water soluble portion of the oil dissolves into the liquid hydrosphere and the lighter fractions evaporate into the atmosphere. In some instances a portion of the oil will adhere to particulate matter and sink. The remaining oil will be subjected to oxidation and bacterial decompositon. Bacteria tend to decompose only the straight-chain, moderate molecular weight hydrocarbon fractions. The heavy molecular weight, branched-chain fractions will sink, once they are freed of the lighter fractions. These heavy fractions form a tarry mass on the ocean floor or at a subsurface depth in the ocean, and are attacked by anaerobic bacteria.[8] The net result, with time, is essentially complete degradation of the spilled oil.

An oil slick is a navigational hazard to sea traffic, a killer of sea birds and a toxic pollutant of marine life. Crude oil and many of the petroleum products cannot be treated as a single pollutant but must be considered as a collection of many substances with different properties and toxicities. Knowledge of the actual toxicity of oil to marine life is limited. Most toxic are the low-boiling point, saturated hydrocarbons and the aromatic hydrocarbons (benzene, toluene, xylene). The concentrations of the various hydrocarbon fractions toxic to the many species of marine life are not known. The most easily observed victims of an oil spill are the marine birds. Very few birds survive contact with an oil slick. The high death rate may be the result of one or a combination of many factors, which include toxicity and increased susceptibility to diseases due to a weakened physical state caused by feather matting, flying difficulties, loss of buoyancy, etc.

Methods of treating oil spills are numerous and vary widely in efficiency. Oil slick treating methods may be classified into two general categories: 1) containment and recovery and 2) dispersion and forced precipitation. Preference is and should be given to containment and recovery methods,if they are feasible. Often, however, the most feasible method of removing an oil slick is by dispersion or forced precipitation.

The methods grouped under containment and recovery include booming, skimming, adsorbing and burning. Booming consists of various methods of fencing the oil spill, the most common being a mechanical, hydrodynamic barrier. The barrier is hydrodynamically designed to maintain an upright orientation with predetermined portions above and below the water line. Booms which have been used range in degree of sophistication from carefully designed structures to fire hoses. Also, worthy of mention is the air bubble-curtain barrier which, when deployed, generates a continuous flow of air bubbles to the surface. The resultant surface tension and turbulence act as a retaining wall to an oil spill. Chemical booming is accomplished by adding a gelling agent to the peripheral oil of a slick. The gelled oil then acts as a barrier to prevent further oil spread.

Skimming is accomplished by pumps with buoyed suctions or by rotating drums which are preferentially oil wet. These drums mount to a recovery vessel which plies the slick collecting the spilled oil.

Adsorbing and recovery are accomplished by spreading the adsorbent over the oil slick and subsequent pick-up of the oil soaked material. Straw and sawdust are often used for this process due to their ready availability.

Burning is seldom attempted because the slick must be ignited immediately after spillage to realize any degree of success. Selective burning of the lighter oil fractions, rapid transfer of heat to the water, and the limited supply of oxygen to the center of the slick are all factors which impede sustained burning of an oil slick.

The major disadvantage of all the containment and recovery methods is their greatly reduced efficiency in the presence of any wave action. The advantage of containment and recovery methods is the removal of the oil from the water, thereby eliminating pollution.

Dispersion and forced precipitation methods leave the oil in the water but dilute it to such an extent that its harmful effects are greatly reduced or nullified. To accomplish dispersion, a surfactant, often in a solvent carrier, is sprayed over the oil spill. The surface is agitated to emulsify the oil, which is thereby dispersed in the water. Forced precipitation is accomplished by dispensing adsorbents, such as treated sand or chalk, over the spill. The oil is adsorbed and sinks with these materials.

The major objection to dispersion and forced precipitation is that the oil remains as a pollutant in the water. When dispersion is chosen as the treatment method, a large volume of emulsifying agent, often nearly equal to the volume of oil being dispersed, is required. In many instances the emulsifier and its carrier solvent have been more toxic to marine life than the spilled oil. When forced precipitation is chosen, a portion of the oil carried to the bottom by the adsorbents is often later released and will reappear on the surface of the water.

There are several advantages to dispersion and forced precipitation methods of treating oil spills. These methods are effective in the presence of wave action and are aided by the wave action imparted in rough seas. Often one of these methods offers the quickest and/or most economical means of treating an oil slick.

3.2 Case History - Summary of Torrey Canyon Catastrophe

A dramatic example of a catastrophic oil spill was provided by grounding of the Torrey Canyon near Land's End, off the southwest coast of England, on March 18, 1967. The Torrey Canyon was a 127,000-ton displacement tanker loaded with 118,000 tons (approximately 900,000 barrels) of Kuwait crude oil. Of the initial 30,000 tons of oil spilled onto the water, 13,000 tons were washed onto the Cornish beaches.[7]

Immediately after the spill, 2,500 tons (500,000 gallons) of detergents were sprayed on the oil slick in an attempt to emulsify and disperse the oil before it got to the beaches. Despite this action nearly half of the initial spill was spread over the beaches. To clean this 13,000 tons of oil from the beaches, 10,000 tons (two million gallons) of detergent were used. A fleet of 42 ships was used to dispense the total 12,500 tons of detergent. A major problem encountered as a result of using emulsifiers was the formation of a water-in-oil emulsion rather than the desired oil-in-water emulsion. The French estimate that by the time the emulsified oil reached their coast the mass had increased to as much as 600,000 tons[9] as a result of the sea water dispersed within the oil. This emulsion behaved quite differently from a normal oil slick. It was a sticky mass which floated as a thick mat on the water and coated everything it contacted. Rather than remain on the surface of the beach as oil normally does, this emulsion penetrated the sand to a depth of as much as 12 inches.

When an attempted salvage operation was unsuccessful, it was decided to try in situ burning of the unspilled portion of the Torrey Canyon cargo. In attempts to ignite and sustain burning of the oil; 160,000 pounds of high explosives (rockets and bombs), 10,000 gallons of aviation kerosene and 3,000 gallons of napalm were used.[10] In situ burning destroyed 60,000 to 75,000 tons, a little more than 1/3 of the oil.[7]

The costs and damages caused by the oil spilled from the Torrey Canyon include 7.2 million dollars paid to the British and French governments,[11] 0.1 million dollars set aside for miscellaneous unsettled private claims, the loss of approximately 1.5 million dollars worth of oil, the loss of the supertanker, and an estimated 30,000 sea birds killed (primarily guillemots and razorbills[12]) and an unknown kill of marine fauna and flora.

3.3 Problem Definition

The Federal Water Pollution Control Administration, as the principal United States government agency dealing with water pollution problems, continues to search for preventive and corrective means of pollution abatement. The basic problem which precipitated this study is the continual pollution of seas, waterways and beaches with crude oil and petroleum products spilled from tankers and barges, as a result of accidents and negligent procedures during normal transport and loading operations and in event of collision or grounding.

3.4 Purpose of Project

This project was proposed as an alternate study in response to Federal Water Pollution Control Administration, Department of the Interior, Request for Proposal WA-68-141, "Treatment of Oil Wastes", April 18, 1968. An alternate proposal was made on the assumption that a preventive approach is better than corrective treatment of oil spillage. It was reasoned that if the oil and oil products were emulsified an in oil-in-water emulsion the cost of emulsification and the sacrifice of 3 percent (volume required for minimum external phase of emulsion) of tanker capacity might not be excessive when compared with the costs and damages incurred with major oil spills.

An emulsified cargo appeared to offer several advantages over corrective treatment. The most commonly used corrective treatment is to disperse the spilled oil into the sea using an emulsifying chemical and a jet stream of water. The volume of emulsifier required to disperse spilled oil often equals the volume of the oil spill. Predictions were that an emulsified cargo would:

1. Retard spillage, due to the increased viscosity of the cargo, in the event of normal tanker leakage and minor ruptures.

2. Disperse rapidly into the sea in the event of major spillage, thus never permitting the formation of an oil slick.

3. Be much less toxic to marine flora and fauna due to the low concentration of chemical emulsifier (0.5%).

4. Reduce fire hazard because each droplet of oil is encased in a protective water jacket.

5. Allow increased rate of microbial decomposition and auto-oxidation as a result of oil dispersion and the resultant increase in oil surface area exposure.

6. Increase cargo stability.

7. Reduce cargo evaporation losses.

8. Upgrade product quality as a result of desalting when the continuous phase of the emulsion is removed.

9. Provide relief from potential pollution damage claims and penalties.

10. Make possible a reduction in insurance rates.

Therefore, the purpose of this project was to study the feasibility of producing emulsified oil at a rate comparable with conventional tanker loading rates and to investigate the economic and ecological advantages and disadvantages of handling oil in an emulsified state.

3.5 Scope of Project

To investigate blender design parameters and emulsified oil characteristics, two crude oils and one oil product were chosen. The Zueitina crude oil from Libya is a high-quality, light oil. The Tia Juana Medium crude oil from Venezuela is representative of the more common medium gravity oils. The #6 Fuel Oil is a very heavy, viscous oil consisting primarily of the residuum from refinery distillation vats.

Two different emulsifiers were selected on the basis of their compatibility with sea water and the oils, their cost and availability. These were base neutralized sulfonated nonionics.

Emulsions were prepared in a batch mixer for various tests during the project.

The oils were tested before and after emulsification to determine any product change which may have been caused by the emulsification/demulsification process.

The stability of the emulsions was tested with reference to time and variation of motion and temperature.

The emulsions and oils were comparatively subjected to various tests to determine the degree of increased safety imparted by emulsification.

The toxicity of each emulsion and emulsifier was evaluated, using salt water fish and the procedure specified by "Bioassay Methods for the Evaluation of Acute Toxicity of Industrial Wastewaters and Other Substances to Fish", Standard Methods for the Examination of Water and Wastewater. Twelfth Edition, American Public Health Association, Inc. This procedure was modified to be in accord with the draft copy, dated November 18, 1968, of the FWPCA "Interim Toxicity Procedures".

Ambient temperature evaporation-rate tests were comparatively conducted on the emulsions and oils.

Emulsification unit design was projected using the data collected while running a bench scale model assembled for this contract. An emulsification unit of 100 barrels-per-minute capacity was chosen as the basic unit.

A conceptual design for a terminal system employing one or more of the basic emulsification units was developed.

An economics study was made, giving due consideration to the capital and operating costs of equipment necessary for a typical terminal. Also considered were chemical costs and economic offsets.

Consideration was given to various methods of breaking the emulsion at its destination.

4. SELECTION OF OILS AND PREPARATION AND TESTING OF EMULSIONS

4.1 Selection of Oils

Three oils were selected to provide sampling of a broad range of petroleum liquids - two imported crude oils and one petroleum product. A light, high quality crude, the Zueitina (Libyan) crude oil, was chosen to represent the light crudes and the low boiling point petroleum fractions. The Tia Juana Medium (Venezuelan) crude was selected to represent the more common medium gravity crude oils. #6 fuel oil was chosen as the petroleum product because it is widely used as ship fuel, and with a specific gravity heavier than water, it represents the extreme of heavy petroleum fractions. Characteristics of these three oils are given in the "As Received" columns of Table 4.9-1.

4.2 Preparation of Test Emulsions

Test emulsions were prepared using each of the three oil samples with each of two chemical emulsifiers for a total of six test emulsions. The six test emulsions were prepared in five gallon batches with a three speed, 30 quart Hobart mixer (Figure 4.2-1).

4.2.1 Selection of Emulsifiers

The inexpensive chemical emulsifier class, sulfonated methyl ethyl amines, normally used by the contractor for emulsifying oils, are ionic and not compatible with sea water. Since compatibility with sea water was important, two new emulsifiers were developed for use during this study.

The selection of emulsifiers for use in this study was primarily governed by compatibility with simulated sea water, cost, toxicity and availability. Considering the above mentioned factors, three emulsifiers were selected and submitted to the contractor by the developer of these emulsifiers, Electro-Chem Chess Laboratories of Ft. Worth, Texas. Screening tests by the contractor reduced the number of emulsifiers to two, which were used throughout the study and hereinafter are referred to by their numbers, I-1751 and I-1752.

To prepare an emulsion containing 97 percent hydrocarbon as the internal (dispersed) phase, it was necessary to select a predominately water soluble material which had tendencies to inhibit the mobility of the exterior water phase. These properties could be achieved by the use of nonionic, ethoxylated materials. However, nonionics usually are not salt water tolerant, so a sulfated or sulfonated nonionic was chosen. The base neutralized sulfonated nonionics were used to reduce emulsifier acidity.

Added emulsion stability could be imparted by the addition of a highly polar surfactant. This polarity could be achieved through the use of cationic or anionic materials. The requirement for salt water compatibile, nontoxic materials directed the use of amine oxides or betaines. Addition of sufficient potassium chloride to obtain 0.002 molar KCl in the continuous phase increased the stability of the finished emulsion.

The several emulsifiers tested were various blends based on the above discussion. The two blends chosen for this study were:

I-1751
  N-Alkyl, polyethoxy ammonium sulfate
  N-Alkyl, amido tertiary amine oxide
  Potassium chloride
  Inert solvent

I-1752
  N-Alkyl, polyethoxy ammonium sulfate
  N-Alkyl, amido tertiary amido sulfobetaine
  Potassium chloride
  Inert solvent

4.2.2 Emulsification Procedure

The procedure for emulsification used in this study was a two step method, which first prepares an "emulsion seed", ultrasonically, then gradually blends the bulk of the dispersed (hydrocarbon liquid) phase into the "emulsion seed" to produce the desired emulsion.[1] The "emulsion seed" consists of 30 percent continuous phase (in this project 25 percent water and 5 percent emulsifier) and 70 percent dispersed phase (one of the three oils used in this study). The "emulsion seed" was prepared by agitating the constituents to form a coarse emulsion premix. The premix was then subjected to ultrasonic cavitation provided by a 500 watt, 20 kilohertz, homogenizer horn. A volume of "emulsion seed" (Figure 4.2-2), equivalent to 10 percent of the volume of end product emulsion, was poured into the 30 quart bowl of the Hobart mixer (Figure 4.2-1). With the mixer paddle rotating, the remaining 90 percent of the dispersed phase was blended into "emulsion seed" to produce the finished emulsion (Figure 4.2-3). The mixer speed was varied from high to low during the blending operation.

Test emulsions were prepared by the above described batch process to assure consistent composition for the test emulsions. A continuous flow system employing the same concept was used for bench-scale determinations covered under section 5 of this report.

4.2.3 Emulsion Storage

Five gallons of each test emulsion was prepared. Each batch was stored in two

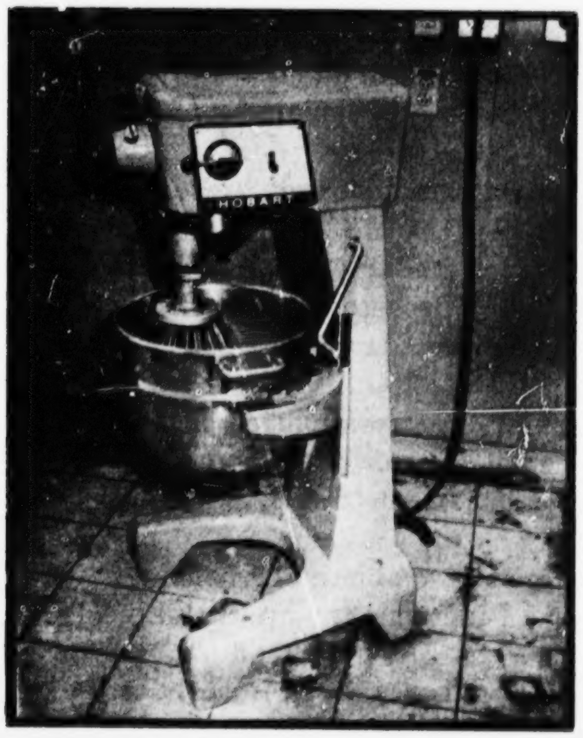


Figure 4.2-1
30-Quart Hobart Mixer

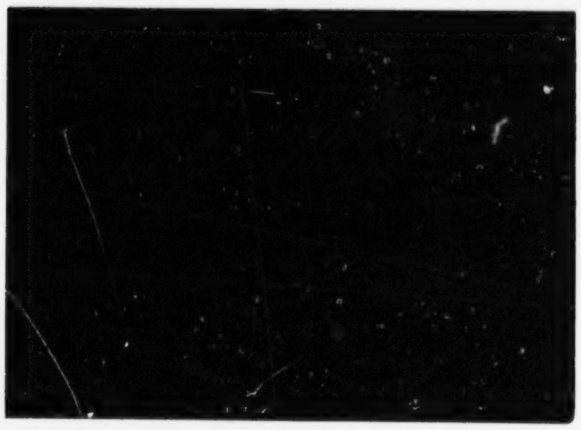


Figure 4.2-2
"Emulsion Seed" (x 210)

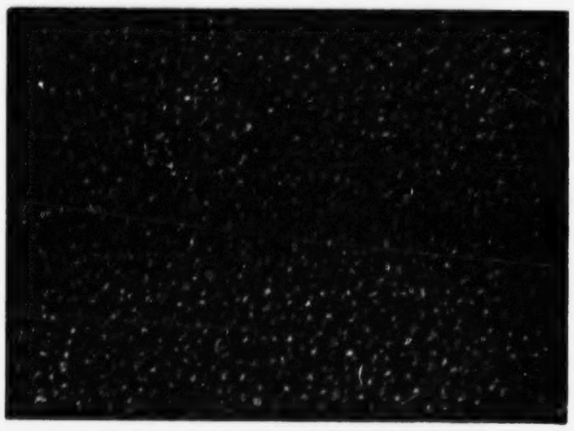


Figure 4.2-3
Finished Emulsion (x 210)

2-gallon jars and six 1-quart jars at 20° C (68° F).

4.3 Emulsion Stability

4.3.1 Method

Long term stability of the emulsions was tested under various conditions for periods in excess of normal transportation times. The test procedure consisted of periodic visual observation and determination of the yield value of each emulsion. Stability was tested under the following conditions:

1. Stability during ambient temperature while quiescent.
2. Stability during - 4° C (25° F) while quiescent.
3. Stability during 50-60° C (122-140° F) while quiescent.
4. Stability during repeated freeze/thaw cycles.
5. Stability under simulated ship motion at ambient temperature.

Visual observations consisted of examination of the emulsion to determine the amount of break-back, stratification and/or changes in physical characteristics. If no visual changes were observed, the emulsion was considered stable.

Emulsion stability was further evaluated by periodic measurement of yield values of the emulsions. A cone penetrometer apparatus, (Figure 4.3-1) specified in ASTM D-217[1] and modified as recommended for use with emulsified fuels[2], was used in these tests. Yield values not significantly different from original values were considered indicative of emulsion stability. For each test or phase of test of temperature and motion stability of the emulsion, a one quart glass jar was filled sufficiently to provide a ten centimeter depth of emulsion. The filled jars were placed in the desired environment and periodic observations and determinations made.

For tests of stability during ambient temperature while quiescent, the test containers were placed on a warehouse shelf where the maximum temperature variation was from 18° to 28° C (64-82° F).

For stability during -4° C (25° F) quiescent tests, the jars were placed in a refrigerator and held at -4° ± 2° C. Yield values were not determined since temperatures were below the pour point of two of the oils.

To determine the stability of the emulsions in a quiescent, elevated temperature environment, the test jars were placed in a test chamber where the temperature was maintained at 50-60° C (122-140° F).

Freeze thaw stability was determined by transferring the test jars between the refrigerator and the elevated temperature chamber. A residence of two days in each chamber was allowed during each four day cycle. Yield values were

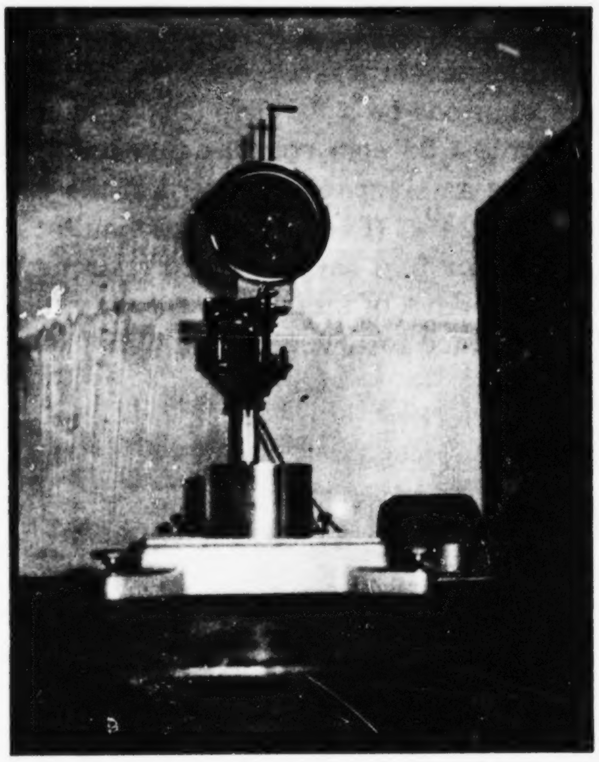


Figure 4.3-1
Cone Penetrometer, Modified

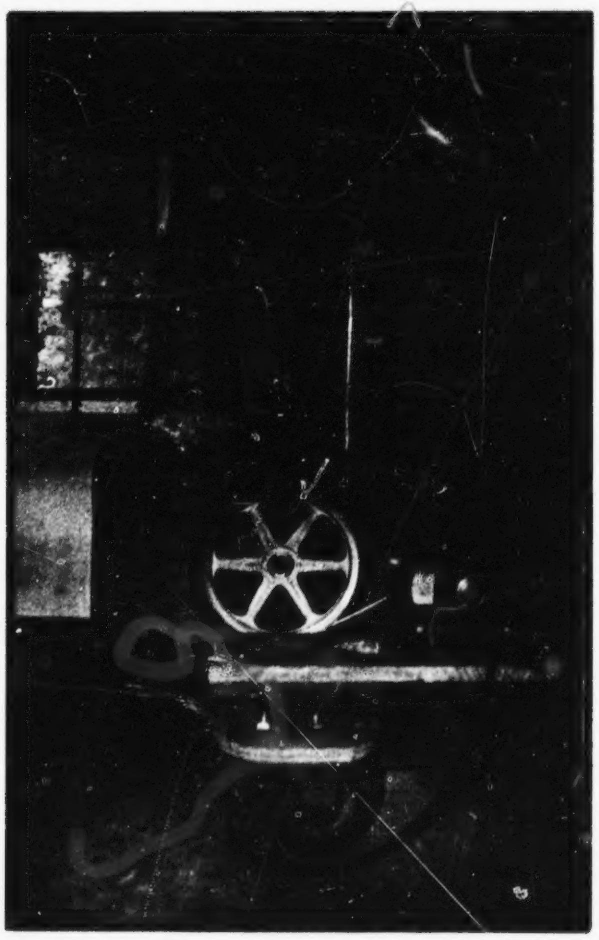


Figure 4.3-2
Motion Apparatus, Modified

determined at the end of each of the five cycles.

Stability during simulated ship motion at ambient temperatures was determined by placing the test jars in a box which was clamped on a Ro-Tap sieve shaker (Figure 4.3-2) that was geared down to provide a 56 rpm rotation through a circular pattern with a 1 1/4 inch diameter. The ambient temperature of the room housing the Ro-Tap machine varied from 18 to 28° C (64-82° F). The emulsions were allowed to relax by undisturbed standing for five days prior to starting the ship motion stability test. After 20 continuous days of simulated ship motion, the emulsions were allowed two days of quiescence followed by eight additional days of resumed ship motion.

4.3.2 Emulsion Stability Data

Table 4.3-1 presents the data collected during the above described stability testing.

Figures 4.3-3 through 4.3-5 are graphic presentations of the yield stability during ambient temperature quiescence. Figures 4.3-6 through 4.3-8 are graphic presentations of emulsion yield stability at 50-60° C (122-140° F) in a quiescent environment. Figures 4.3-9 through 4.3-11 are graphic presentations of the emulsion yield stability during five four day freeze/thaw cycles. Figures 4.3-12 through 4.3-14 are graphic presentations of emulsion stability during simulated ship motion at ambient temperature.

4.3.3 Discussion of Emulsion Stability

When subjected to a quiescent environment with an ambient temperature of 18 to 28° C (64-82° F) for ninety days, the emulsion remained stable. (Figures 4.3-3 to 4.3-5). The crude oil emulsions sustained a continual, slow relaxation, which was reflected as a gradual reduction in yield value. The relaxation was never complete enough to allow phase separation, that is, the formation of free oil. The #6 Fuel Oil emulsion relaxed less than the crude oil emulsions because it was made with 0.8 percent emulsifier rather than 0.5 percent used to make the crude oil emulsions. Nixon, Philippoff and Siminski [3] found that the initial yield and the yield stability increased with increases in the amount of emulsifier used to form a jet fuel emulsion.

These emulsions were relatively stable in a cold (-4° C), quiescent environment. Yield value determinations were not made during these tests. However, all six emulsions were "stiffer" in the chilled state - especially the Zuietina crude and #6 Fuel Oil emulsions. This increased emulsion stiffness can be attributed primarily to the increase in oil viscosity, reflected by the high pour point of the oils. These tests were conducted at a temperature considerably below the pour point of both the Zueitina crude and the #6 Fuel Oil (see Table 4.9-1 for the characteristics of oil samples). The Tia Juana medium crude emulsified with I-1751

TABLE 4.3-1

EMULSION STABILITY AS INDICATED BY YIELD VALUES

	Emulsion Yield Values (dynes/cm^2)					
Stability Test	Zueitina with		Tia Juana with		# 6 Fuel Oil with	
	I-1751	I-1752	I-1751	I-1752	I-1751	I-1752
Initial	600	500	600	550	1,800	1,550
Ambient Temperature, Quiescent						
1 hour	600	530	600	550	1,800	1,550
1 day	590	510	560	500	1,800	1,550
10 days	590	500	550	490	1,800	1,500
30 days	580	500	540	470	1,800	1,500
60 days	580	500	520	440	1,800	1,500
90 days	570	490	510	400	1,750	1,500
-4°C, Quiescent						
1 day	Stable	Stable	Stable	Stable	Stable	Stable
10 days	Stable	Stable	Stable	Stable	Stable	Stable
30 days	Stable	Stable	Trace of free oil	Stable	Stable	Stable
60 days	Stable	Stable	Broken	Stable	Stable	Stable
50-60°C, Quiescent						
1 day	590	500	560	500	1,750	1,500
10 days	580	490	540	480	1,700	1,450
30 days	560	460	510	440	1,600	1,400
Freeze/Thaw Cycles (4 days per cycle)						
1 cycle	580	500	550	500	1,750	1,500
2 cycles	560	490	530	480	1,750	1,500
3 cycles	530	470	500	460	1,700	1,450
4 cycles	500	450	460	430	1,700	1,450
5 cycles	460	420	Trace of free oil	400	1,650	1,450
Simulated Ship Motion, Ambient Temperature						
Relaxed	590	510	560	500	1,800	1,500
1 day	600	510	570	510	1,800	1,500
5 days	600	520	570	510	1,800	1,500
10 days	600	520	570	510	1,800	1,500
20 days	600	520	570	510	1,800	1,500
30 days	600	520	570	510	1,800	1,500

FIGURE 4.3- 3
STABILITY TO AMBIENT TEMPERATURE QUIESCENCE

ZUEITINA EMULSIONS

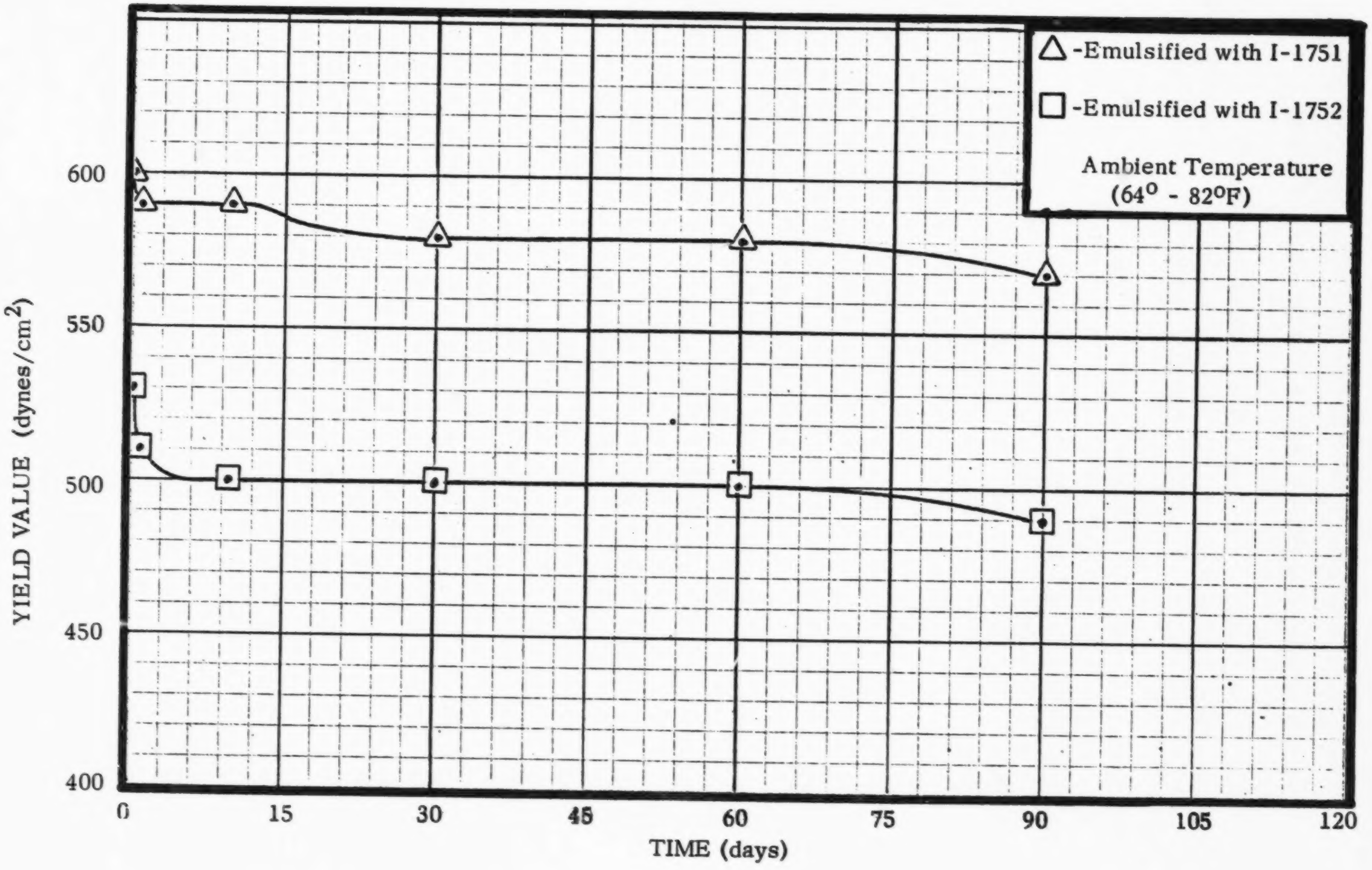


FIGURE 4.3-4
STABILITY TO AMBIENT TEMPERATURE QUIESCENCE
TIA JUANA EMULSIONS

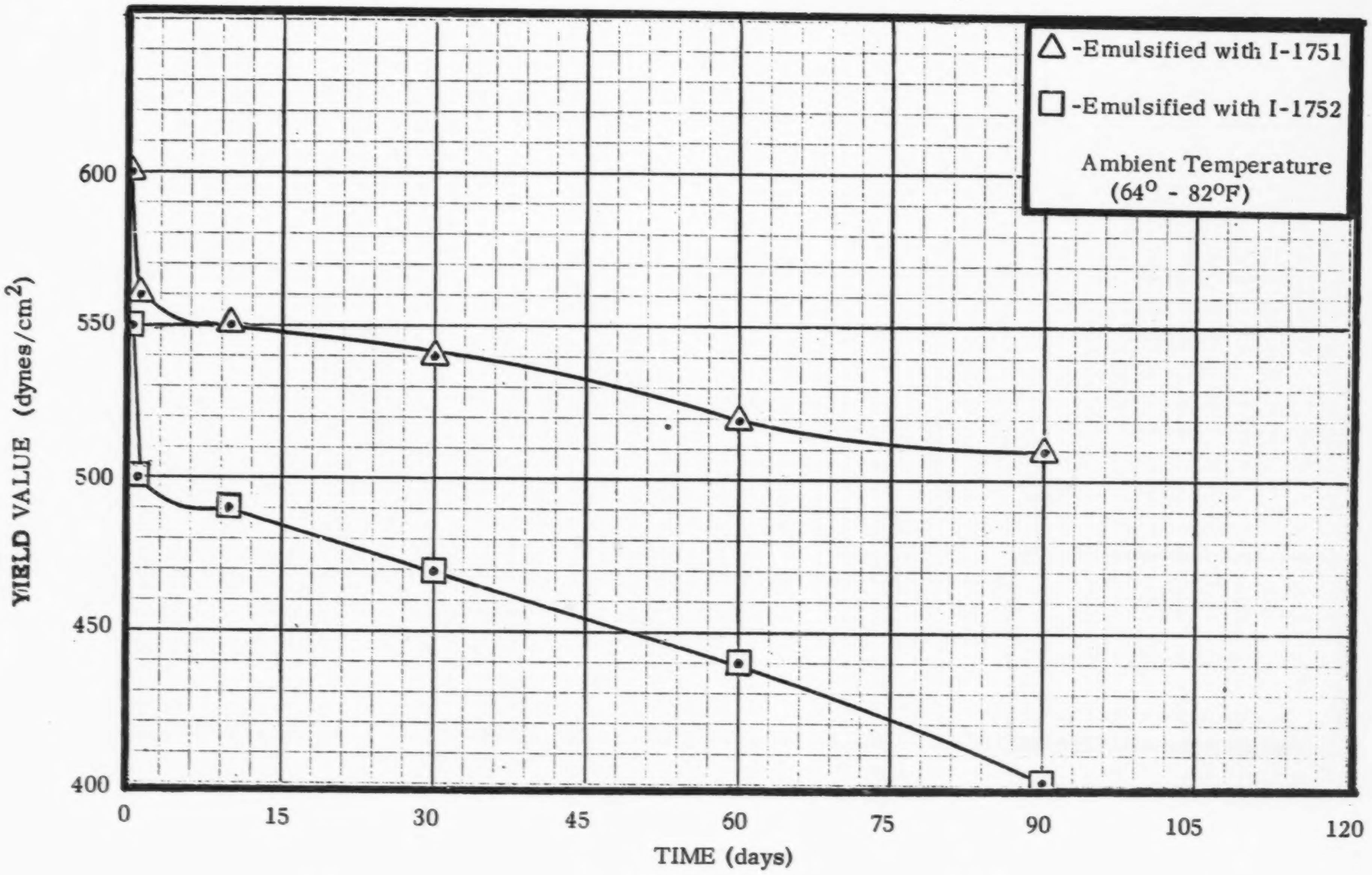


FIGURE 4.3-5
STABILITY TO AMBIENT TEMPERATURE QUIESCENCE

#6 FUEL OIL EMULSIONS

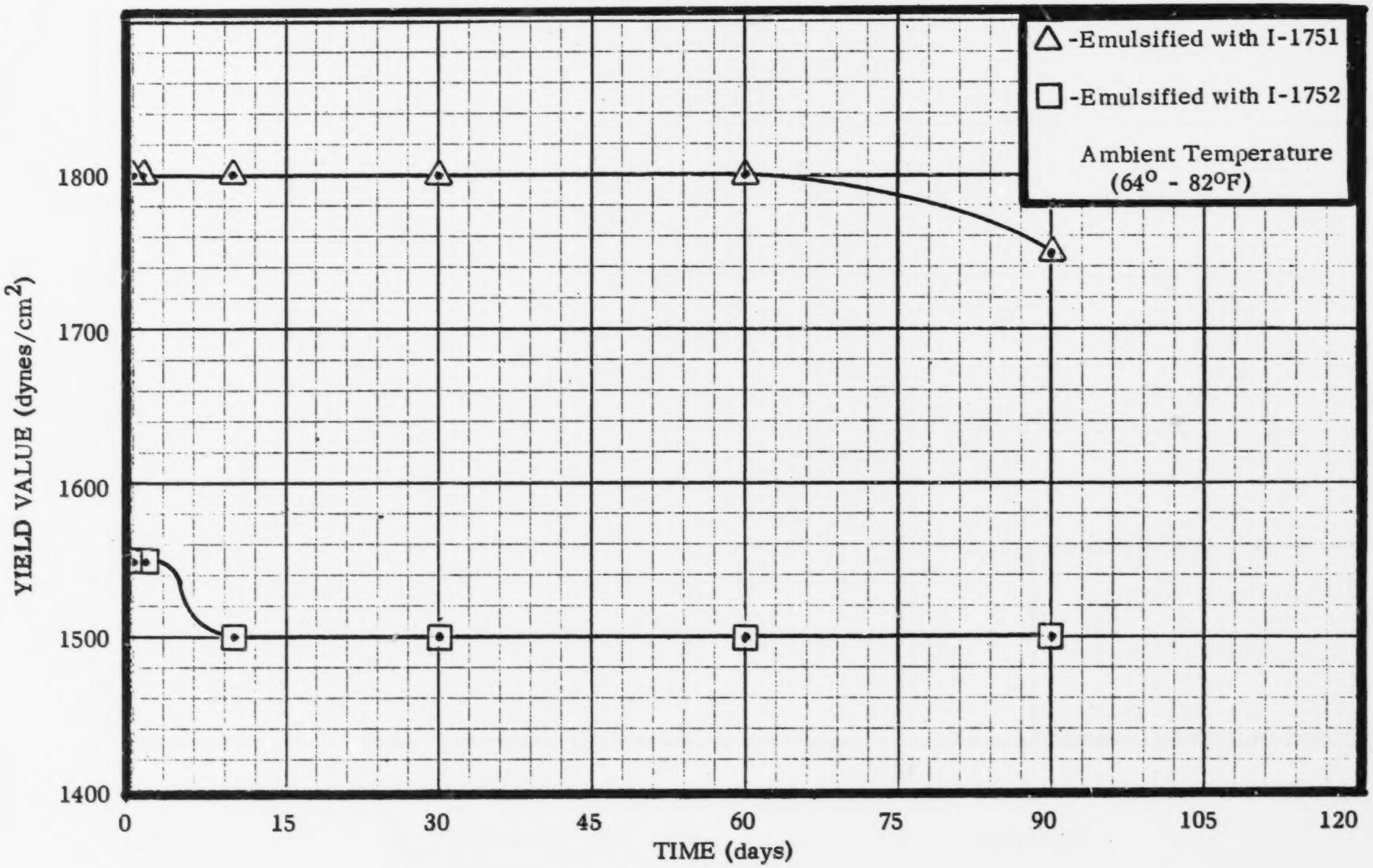


FIGURE 4.3-6
STABILTIY TO 50° - 60° C QUIESCENCE
ZUEITINA EMULSIONS

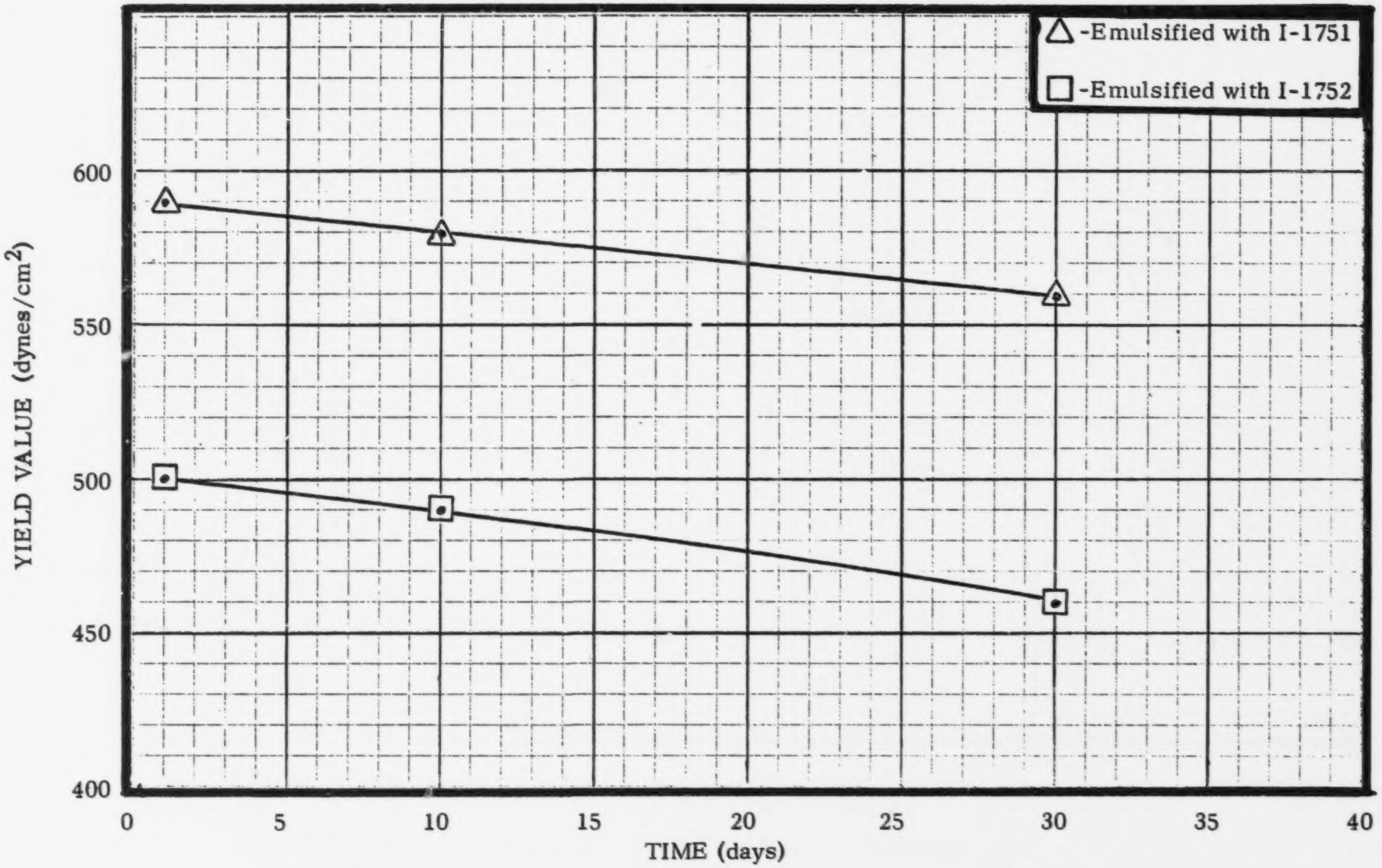


FIGURE 4.3-7
STABILITY TO 50° - 60° QUIESCENCE
TIA JUANA EMULSIONS

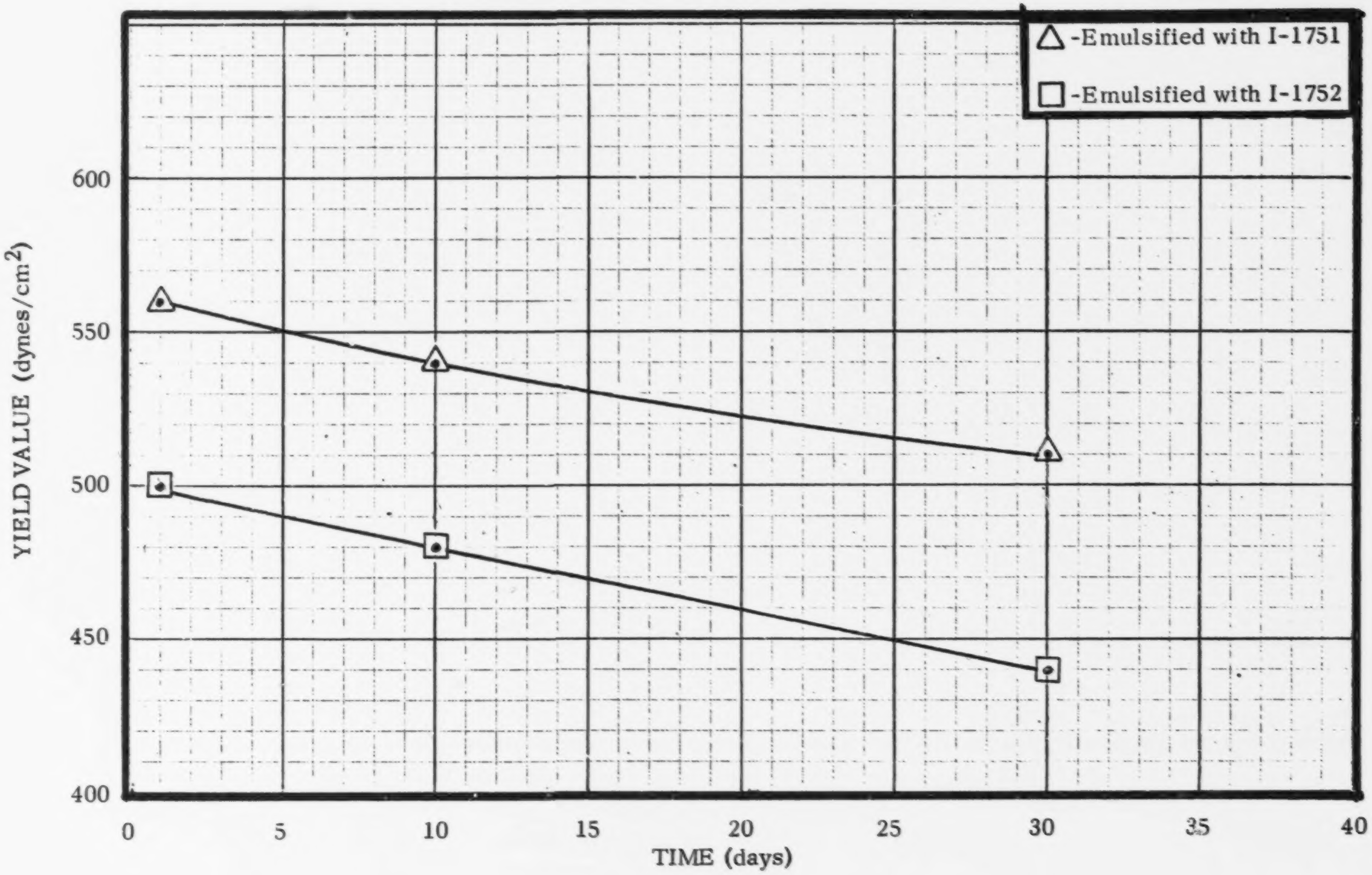


FIGURE 4.3-8
STABILITY TO 50° - 60°C QUIESCENCE

6 FUEL OIL EMULSIONS

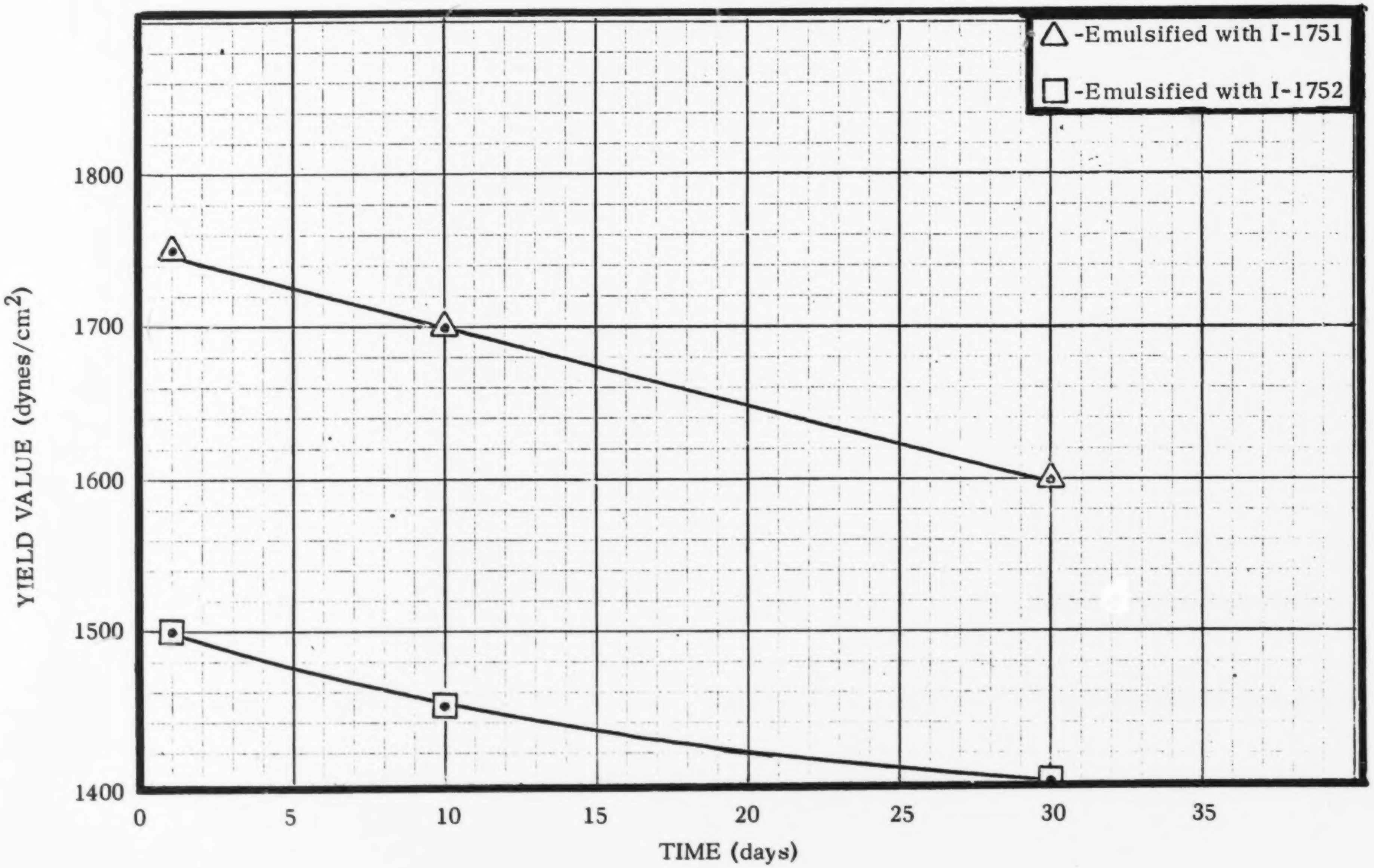


FIGURE 4.3-9
STABILITY TO FREEZE-THAW CYCLES
ZUEITINA EMULSIONS

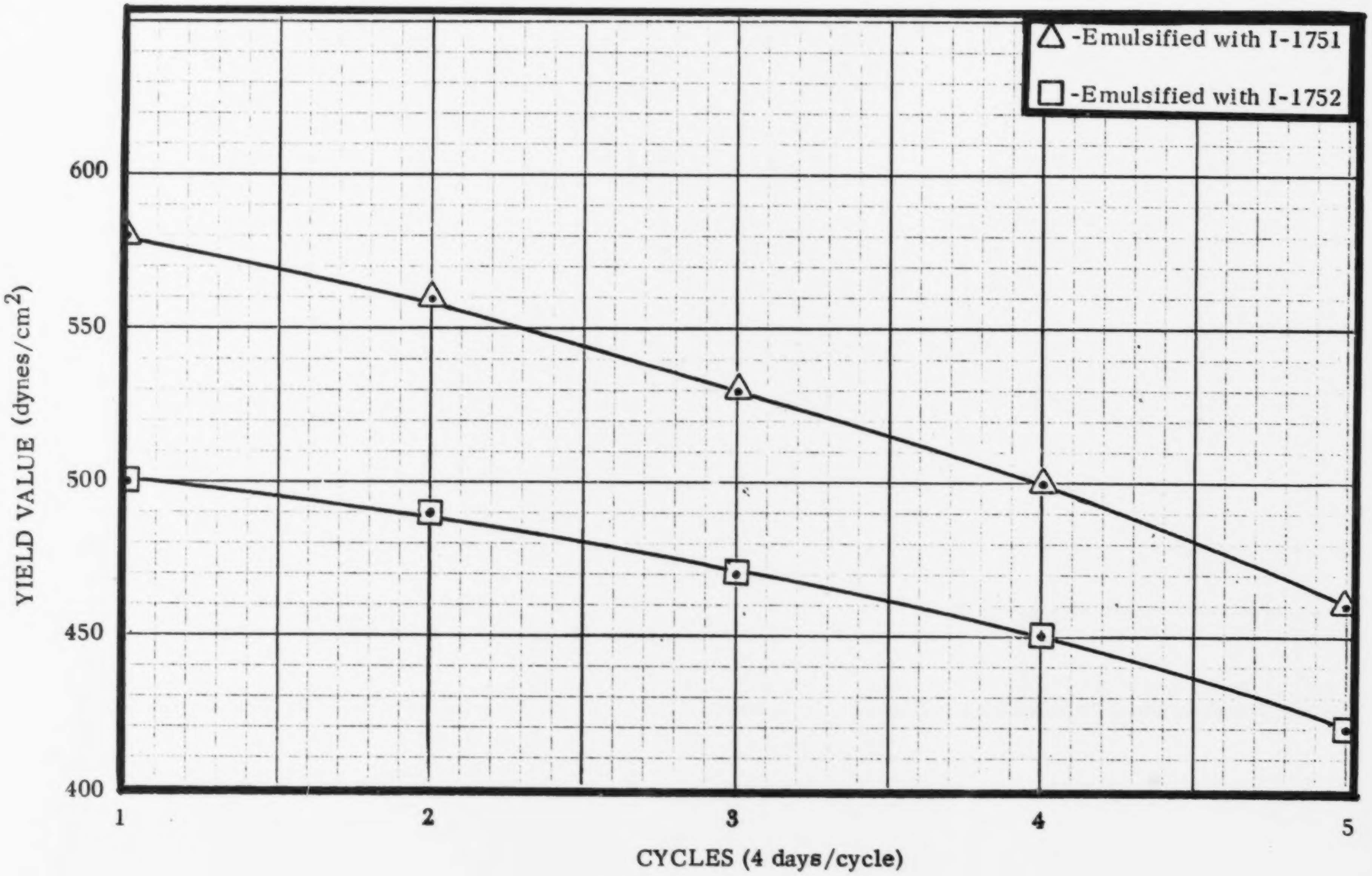


FIGURE 4.3-10
STABILITY TO FREEZE-THAW CYCLES

TIA JUANA EMULSIONS

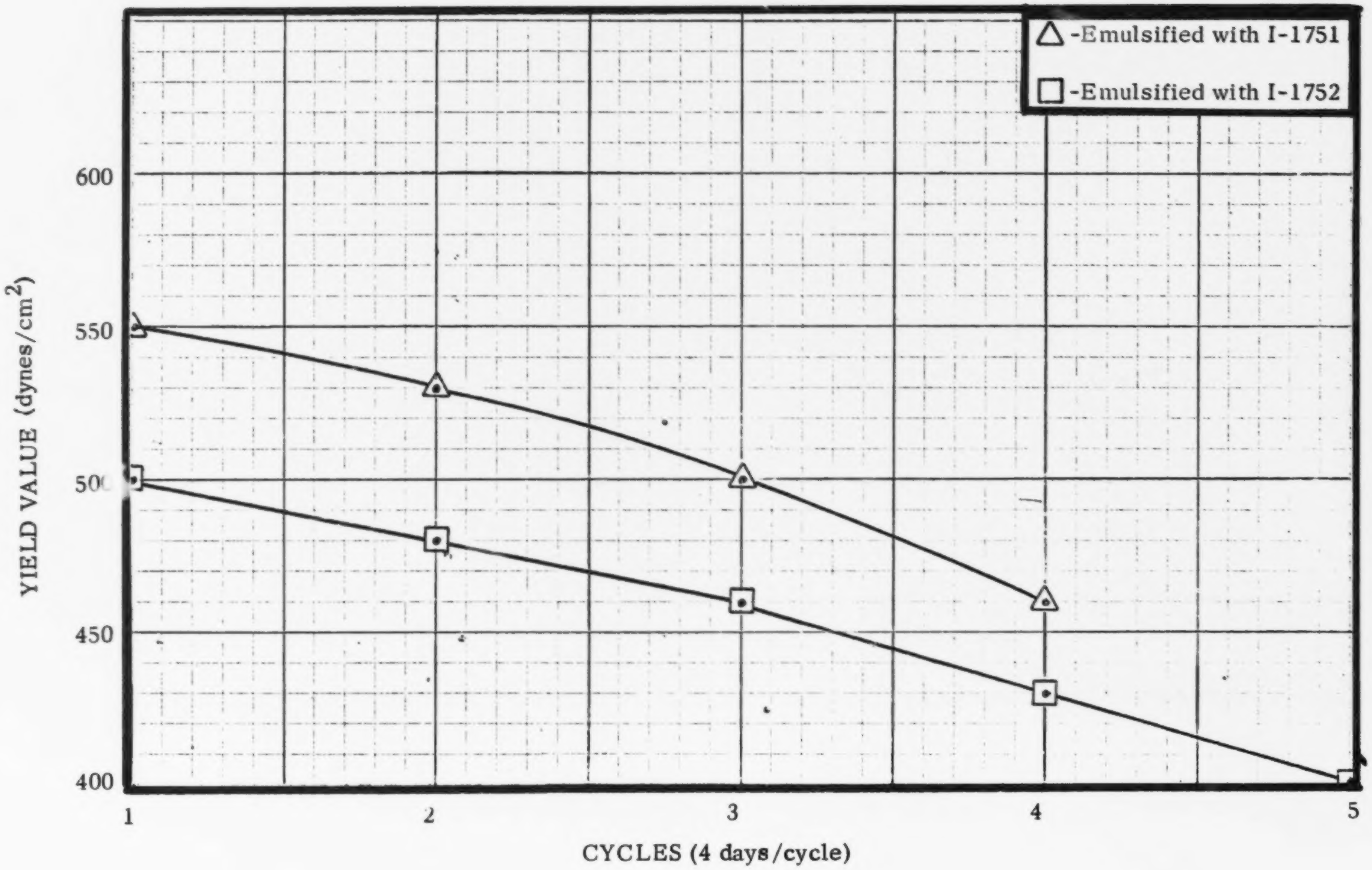


FIGURE 4.3-11
STABILITY TO FREEZE-THAW CYCLES

6 FUEL OIL EMULSIONS

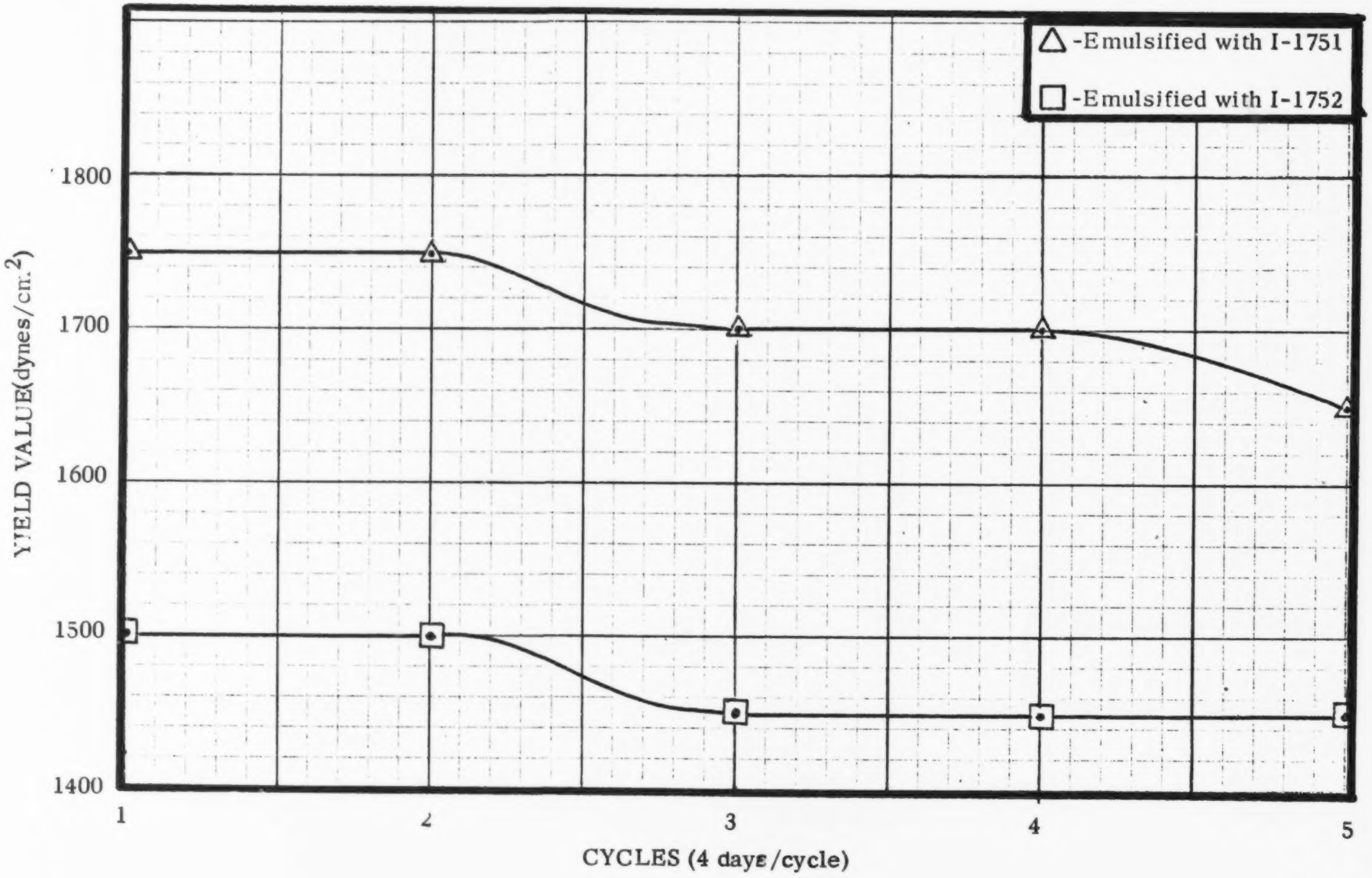


FIGURE 4.3-12
SHIP MOTION STABILITY
ZUEITINA EMULSIONS

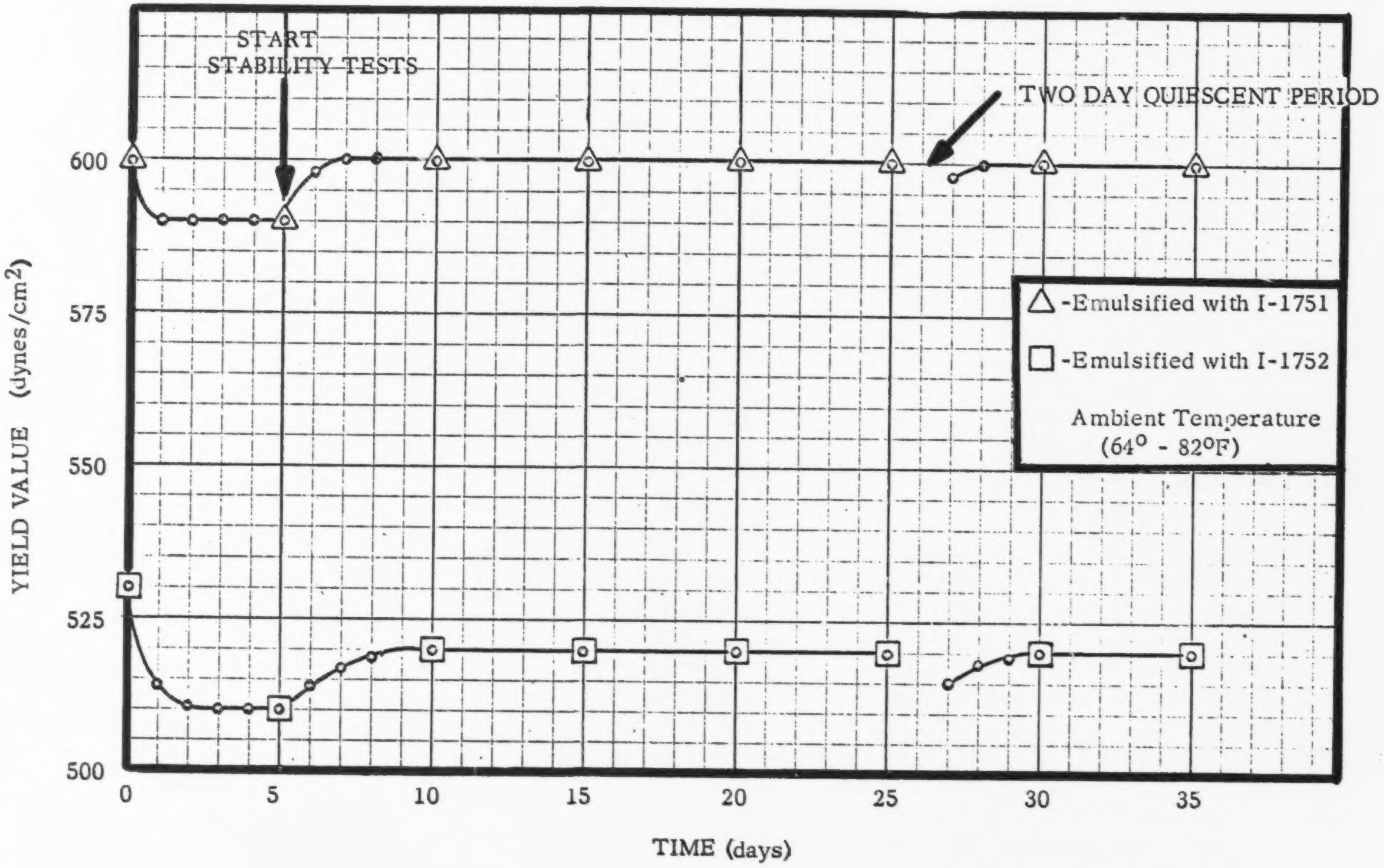


FIGURE 4.3-13
SHIP MOTION STABILITY
TIA JUANA EMULSIONS

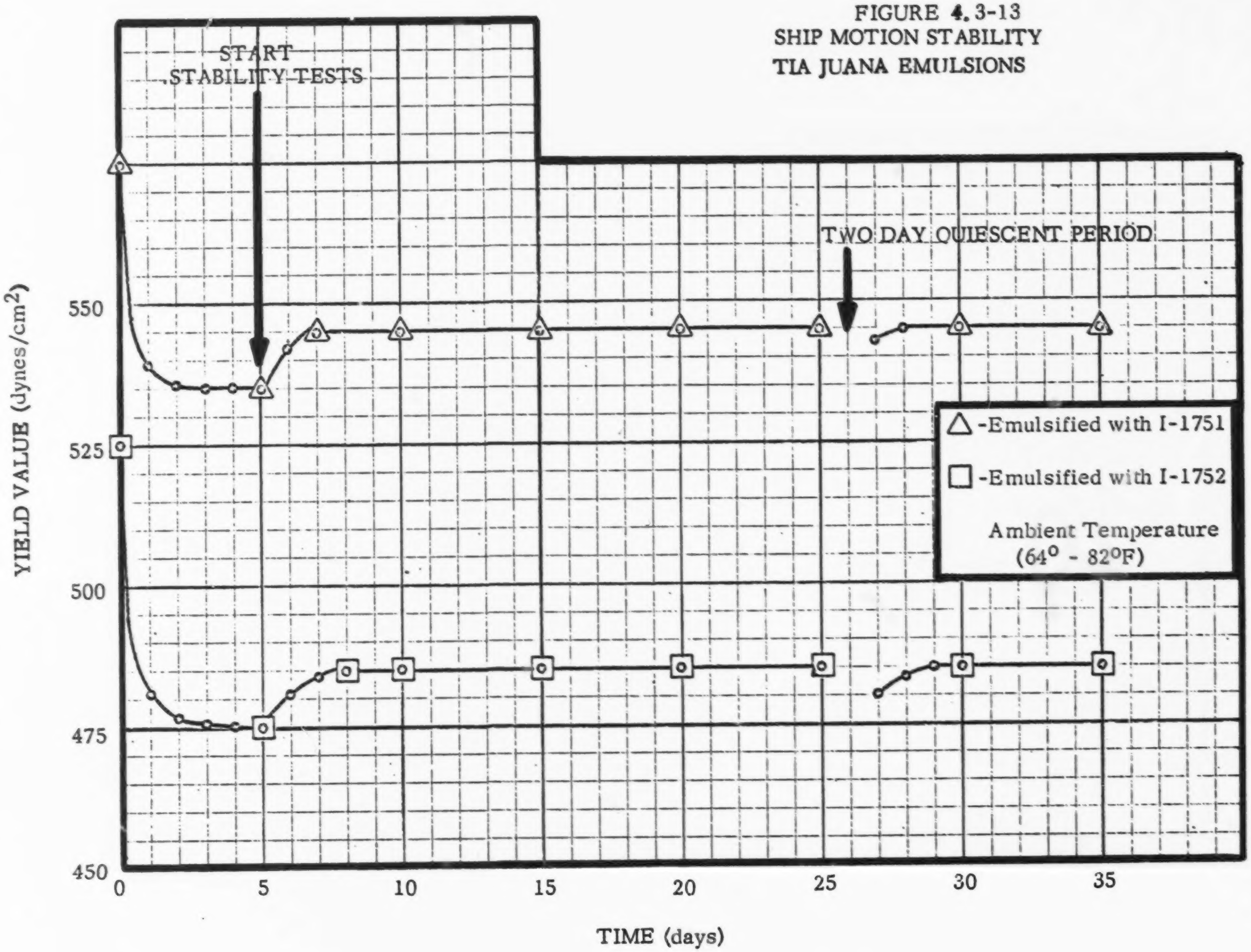
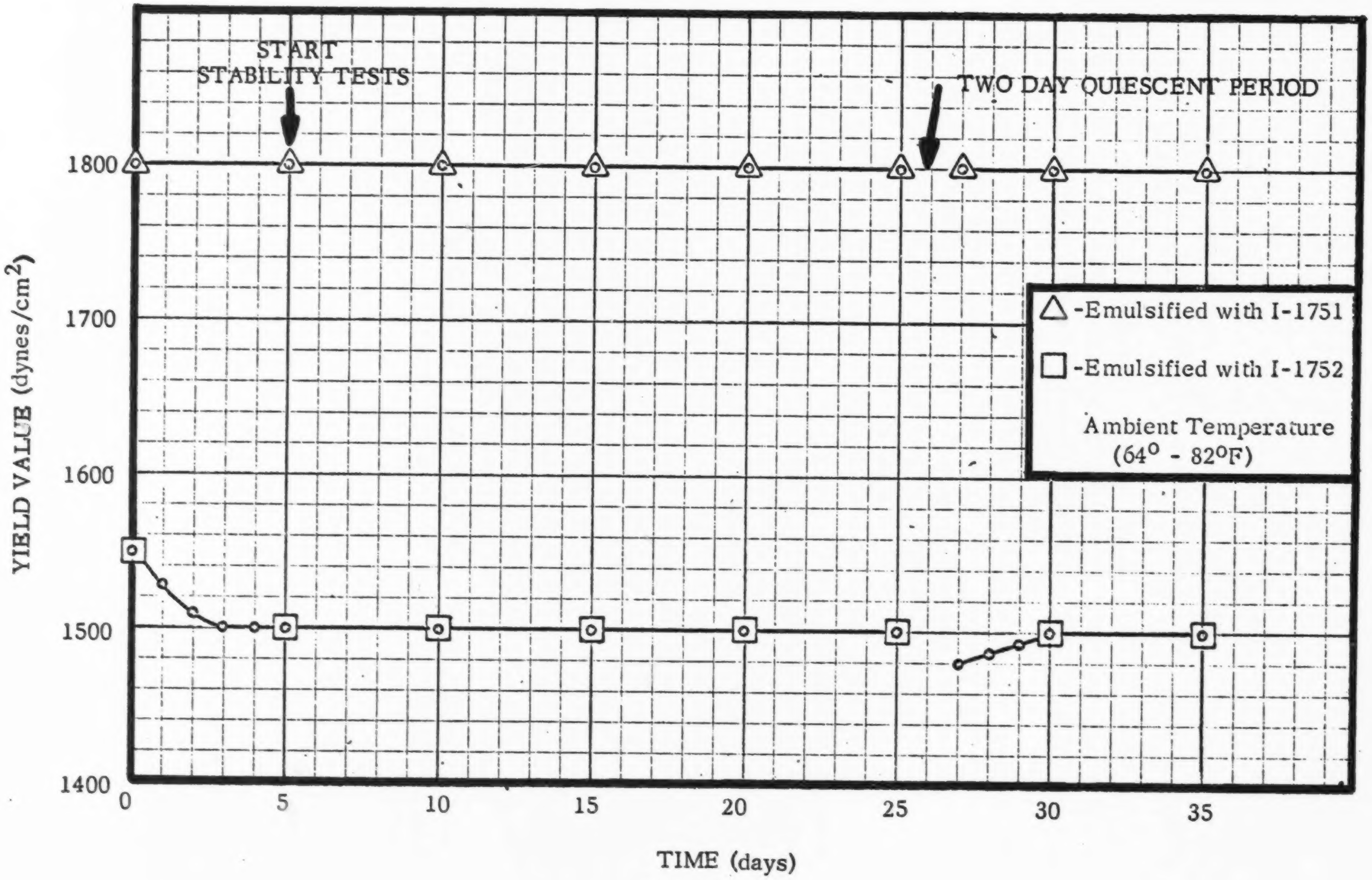


FIGURE 4.3-14
SHIP MOTION STABILITY
6 FUEL OIL EMULSIONS



was the only emulsion to break and separate into its constituent phases during these tests.

All six emulsions remained stable throughout 30 days of exposure to elevated temperature ($50-60^{\circ}C$) quiescent (Figures 4.3-6 through 4.3-8). As expected, the emulsions relaxed much more rapidly in an elevated temperature environment that in the ambient temperature environment.

Test emulsions were generally stable to repeated freeze/thaw cycles (Figures 4.3-9 through 4.3-11). The freeze/thaw cycles caused the most rapid rate of emulsion relaxation observed during emulsion stability testing.

The stability of each emulsion was enhanced by simulated ship motion (Figures 4.3-12 through 4.3-14). The emulsions had higher yield values after five days of simulated ship motion than after five days of quiescent relaxation. These higher yields were maintained as long as the simulated ship motion continued.

In conclusion, the emulsion stability determinations revealed satisfactory stability, in a quiescent environment, over a broad range of temperatures. Gentle agitation, provided by simulated ship motion, improved emulsion stability.

4.4 Dispersion of Emulsion in Sea Water

4.4.1 Method

To determine the stability of a high concentration of dispersed emulsion such as would be expected in the immediate vicinity of a major spill, a one percent (by volume) solution of emulsion in the standard, synthetic sea water (see Section 4.7.3 for a discussion of standard sea water) was placed on the test apparatus for simulated wave motion (described in Section 4.3.1) for a period of 96 hours.

Each test sample was prepared by adding 5 milliliters of emulsion to 495 milliliters of standard sea water in a one quart glass container. Each container was shaken to achieve complete dispersion of the emulsion. The dispersed emulsion was then allowed to stand undisturbed for one hour, after which visual observations were made for any indications of break-out of free oil.

After recording the one hour observations, each sample was placed on the test unit which provided a constant gentle agitation comparable to that of a calm sea. Visual observation of the dispersed emulsions were recorded after 24, 48 and 96 hours of agitation. The visual observations consisted of determining the percent of the five milliliter charge emulsion which was present as free oil, as floating emulsion (as a concentration of emulsion which collected near the surface of the water, but could be redispersed by stirring or more vigorous agitation than that provided by the simulated wave motion) and as uniformly dispersed emulsion. Also recorded were any unusual phenomena.

The same method, using 0.5 milliliters of emulsion in 499.5 milliliters of standard sea water, as described above was used for a 0.1 percent, or 1,000 parts per million solution. Also considered was the behavior of the emulsion dispersed at various concentrations for the toxicity determinations (Section 4.7).

4.4.2 Emulsion Dispersion Data

Test results using the one percent dispersion determinations are presented in Table 4.4-1 and Figures 4.4-1 through 4.4-3. Test results with the 0.1 percent determinations are presented in Table 4.4-2 and Figures 4.4-4 through 4.4-6. Observations on emulsion dispersion during toxicity testing were taken from the laboratory notes and incorporated in Section 4.4.3 Discussion of Emulsion Dispersion.

4.4.3 Discussion of Emulsion Dispersion

The concentration of dispersed emulsion would be relatively high in the immediate vicinity of a major emulsified oil spill on the open sea. A short distance (a few inches) from the spilled emulsion, the concentration would be about one percent or 10,000 parts per million. The concentration would rapidly diminish to 0.1 percent, or 1,000 parts per million. This rapid dispersion would result from the tendency of the minute oil droplets (1 to 10 microns in diameter) to be released and repelled by the emulsion mass as a result of the surface tension phenomena encountered when emulsions of the type used in this study are brought into contact with water. The tendency of the emulsion to disperse would be aided by wind and wave action.

In the one percent dispersion tests (Table 4.4-1 and Figures 4.4-1 through 4.4-3), the two crude oil emulsions formed a dispersion within this confined volume, which was stable and remained uniformly dispersed during one hour of quiescence. One hour would be sufficient time for the emulsion to be extensively dispersed in a normal sea environment. The crude oil emulsions displayed remarkable dispersion stability in the presence of mild agitation for two days. After 24 hours of simulated wave motion, less than five percent of the dispersed charge emulsion had coalesced to form free oil. The remaining 95+ percent was still dispersed or present as a floating emulsion which could be readily redispersed with a slightly more intense agitation than that provided by the shake tester. After 48 hours, only 10 percent of the dispersed emulsion had formed as free oil. After 96 hours, 70 to 80 percent of the emulsion was present as free oil.

The one percent solution of #6 Fuel Oil emulsion was much more difficult to disperse and keep dispersed than the crude oil emulsions. After one hour of quiescence one-half of the #6 Fuel Oil emulsion was dispersed and the other half was a floating emulsion which was not easily redispersed. As the emulsion coalesced, it entrapped considerable free water and formed "balls" on the water surface. After 96 hours of simulated wave motion, 70 percent of the emulsion was present

TABLE 4.4-1
TIME STABILITY OF 1% DISPERSED EMULSION

TIME AFTER START (hours)	PORTION OF CHARGE EMULSION (%)																	
	Zueitina Emulsified With						Tia Juana Emulsified With						#6 Fuel Oil Emulsified With					
	I-1751			I-1752			I-1751			I-1752			I-1751			I-1752		
	FO	FE	DE	FO	FE	DE	FO	FE	DE	FO	FE	DE	FO	FE	DE	FO	FE	DE
0	0	0	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0	100
1	0	0	100	0	0	100	0	0	100	0	0	100	0	50	50	0	20	80
24	5	50	45	tr*	40	60	tr*	30	70	5	40	55	30	40	30	20	20	60
48	30	50	20	10	50	40	10	35	55	10	40	50	60	30	10	40	30	30
96	80	10	10	70	20	10	70	25	5	70	20	10	70	30	0	70	30	tr*

FO = Free Oil
FE = Floating Emulsion
DE = Dispersed Emulsion

* tr = trace (less than 1%)

FIGURE 4.4-1
TIME STABILITY OF 1% DISPERSED EMULSION

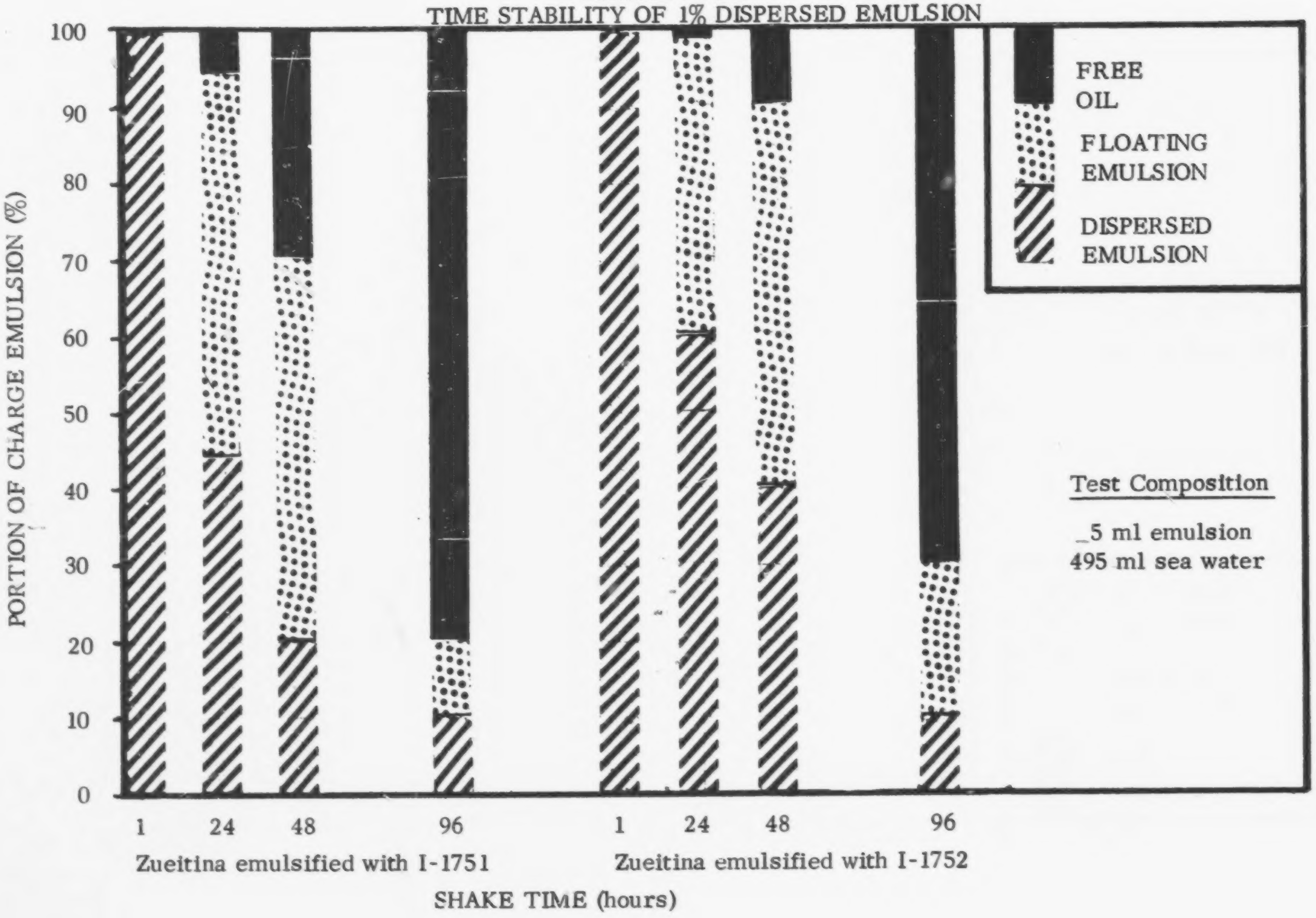


FIGURE 4.4-2
TIME STABILITY OF 1% DISPERSED EMULSION

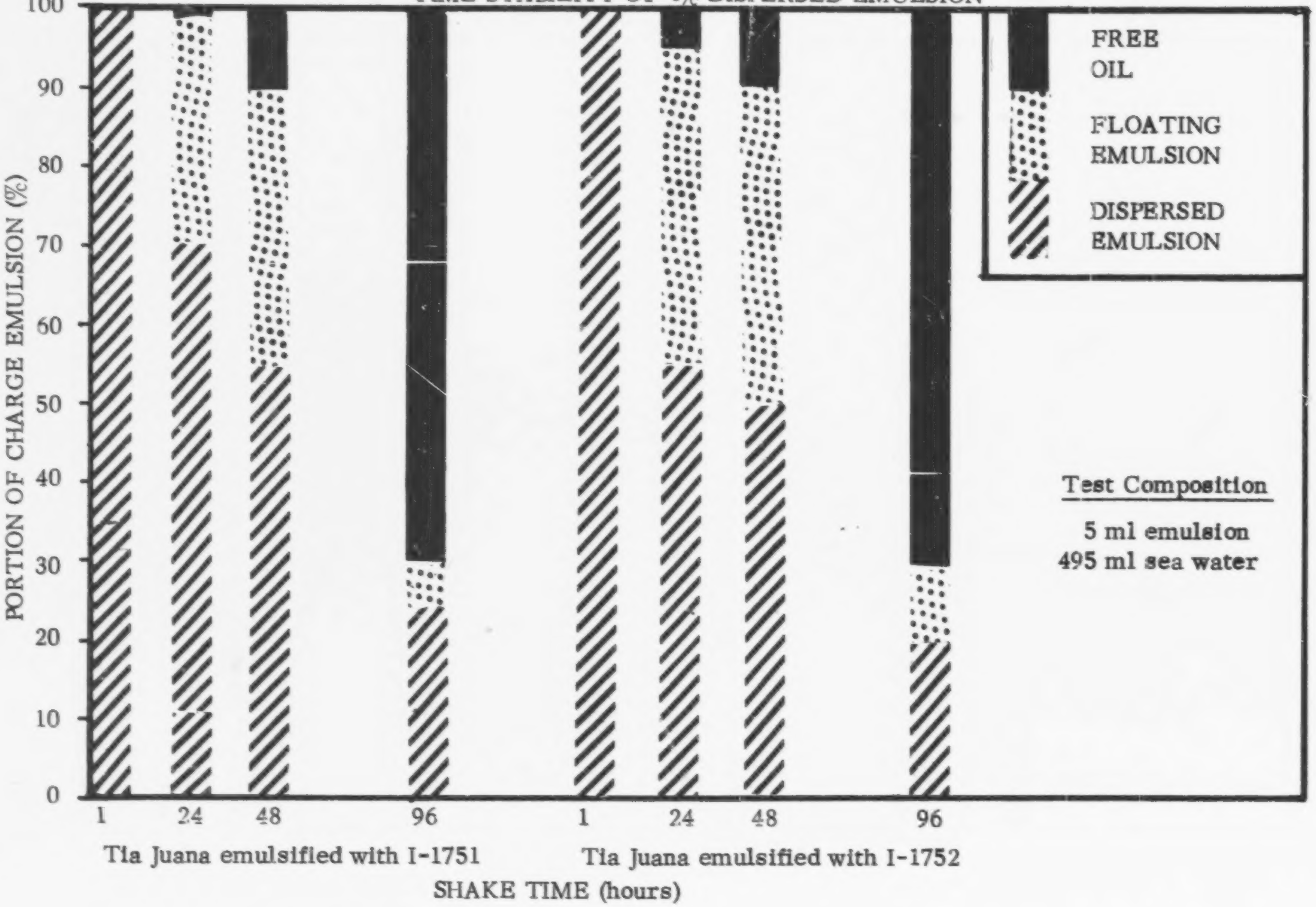
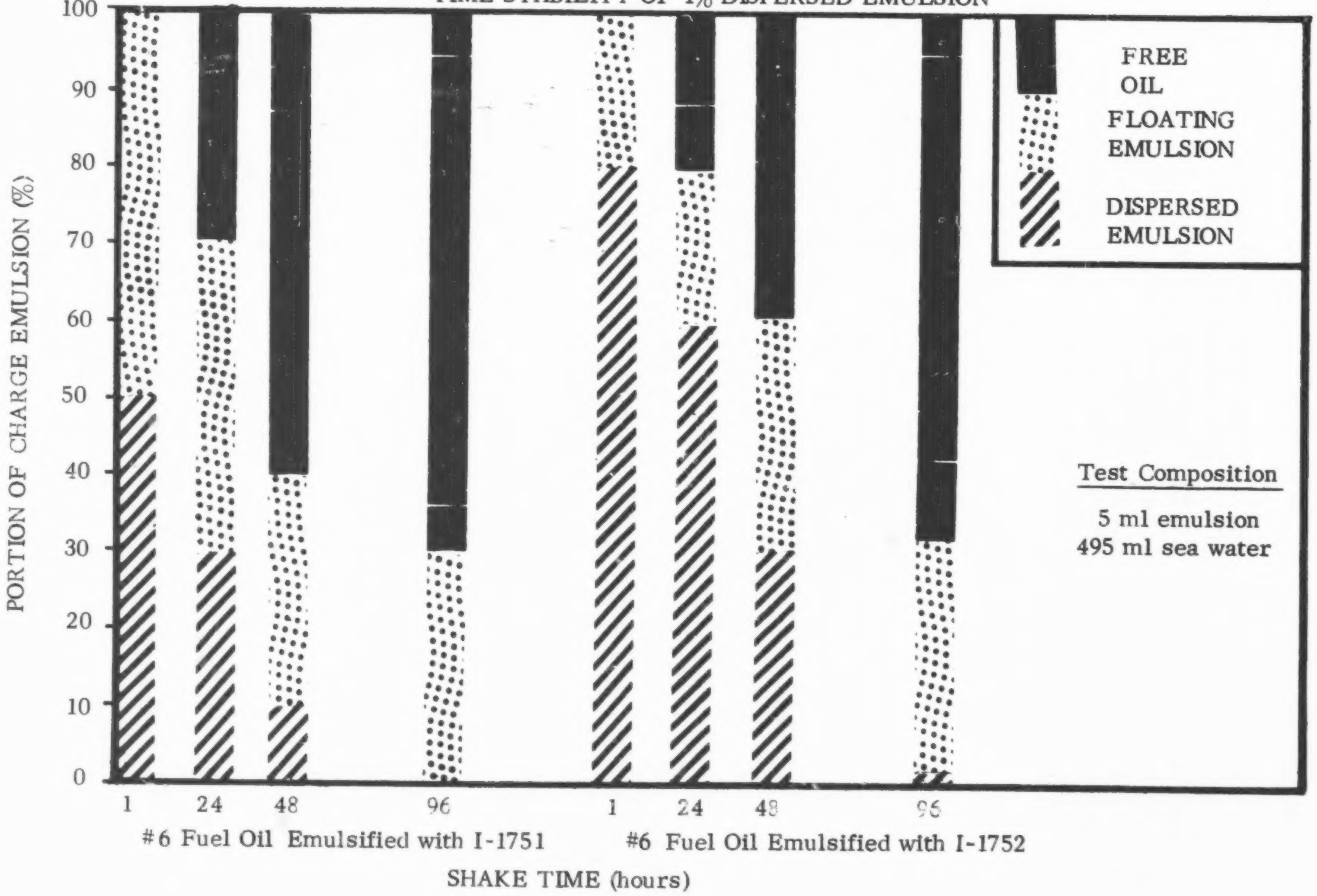


FIGURE 4.4-3
TIME STABILITY OF 1% DISPERSED EMULSION



as floating masses of water-in-oil emulsion.

In the 0.1 percent (1,000 parts per million) dispersion tests (Table 4.4-2 and Figures 4.4-4 through 4.4-6) all three emulsions formed stable dispersions. The Zueitina emulsions formed dispersions which were stable for two days of motion testing, and showed only slight tendencies to stratify after 96 hours. The Tia Juana and #6 Fuel Oil emulsions formed stable dispersions for one day, displayed tendencies toward stratification after the second day, and had begun to form free oil after 96 hours on the motion tester.

During the 96 hour toxicity tests, the emulsions all remained well dispersed at all concentrations below 600 parts per million. Above 600 parts per million, the Tia Juana and #6 Fuel Oil emulsion dispersions had tendencies to stratify after 48 hours, thus allowing portions of the emulsions to float to the surface. In the case of the dispersed Tia Juana emulsion, this floating emulsion was easily redispersed by additional hand stirring with a glass rod. The dispersed #6 Fuel Oil emulsions developed a trace of free oil, which would not redisperse, on the water surface. After 96 hours, free oil was present as a uniform thin film. There was no "balling" or coalescence of the #6 Fuel Oil emulsion as was observed in the dispersion tests.

As the emulsion disperses, the emulsifier, which is primarily hydrophilic, is diluted with water and freed from the oil droplets. As the emulsifier is lost, the droplets become widely separated so that there is little tendency to coalesce, even with no emulsifier remaining. For example, assume a spill, creating a mass of emulsified oil, from which emulsion is being dispersed at a rate of 10,000 barrels per day. Further assume an ocean current of one knot, and that the plume of contaminated water downstream widens at an angle of 10 degrees from the center line and deepens to 250 feet. If the dispersal of one element of emulsion is followed as it is carried away, in one hour the oil concentration will be down to 0.7 milligrams per liter. Thus, it appears likely that, as emulsifier is lost, the droplets will become too widely dispersed to agglomerate. No slick should form under these conditions.

In summary, the dispersed emulsions each displayed a high degree of stability. All data indicate that the emulsions would be so completely dispersed by natural sea forces that the minute droplets of oil would not coalesce to form an oil slick, even though the emulsifiers had been lost due to dilution by sea water. Indications are that the spilled emulsion would be dispersed within a day's time, to a concentration well below the presently accepted 100 parts per million for oily waste waters. At concentrations below 100 parts per million, the oil droplets are so completely dispersed that droplets coalescence would rarely occur.

4.5 Evaporation Rate Tests

TABLE 4.4-2
TIME STABILITY OF 0.1% DISPERSED EMULSION

TIME AFTER START (hours)	PORTION OF CHARGE EMULSION (%)																	
	Zueitina Emulsified With						Tia Juana Emulsified With						#6 Fuel Oil Emulsified With					
	I-1751			I-1752			I-1751			I-1752			I-1751			I-1752		
	FO	FE	DE	FO	FE	DE	FO	FE	DE	FO	FE	DE	FO	FE	DE	FO	FE	DE
0	0	0	100	0	0	100	0	0	100	0	0	100	0	0	100	0	0	100
1	0	0	100	0	0	100	0	0	100	0	0	100	0	10	90	0	10	90
24	0	0	100	0	0	100	0	5	95	0	5	95	0	20	80	0	20	80
48	0	0	100	0	0	100	0	15	85	0	20	80	tr*	35	65	0	40	60
96	0	5	95	0	5	95	tr*	25	75	5	30	65	10	40	50	5	50	45

FO = Free Oil
FE = Floating Emulsion
DE = Dispersed Emulsion

*tr = trace (less than 1%)

FIGURE 4.4-4
TIME STABILITY OF 0.1% DISPERSED EMULSION

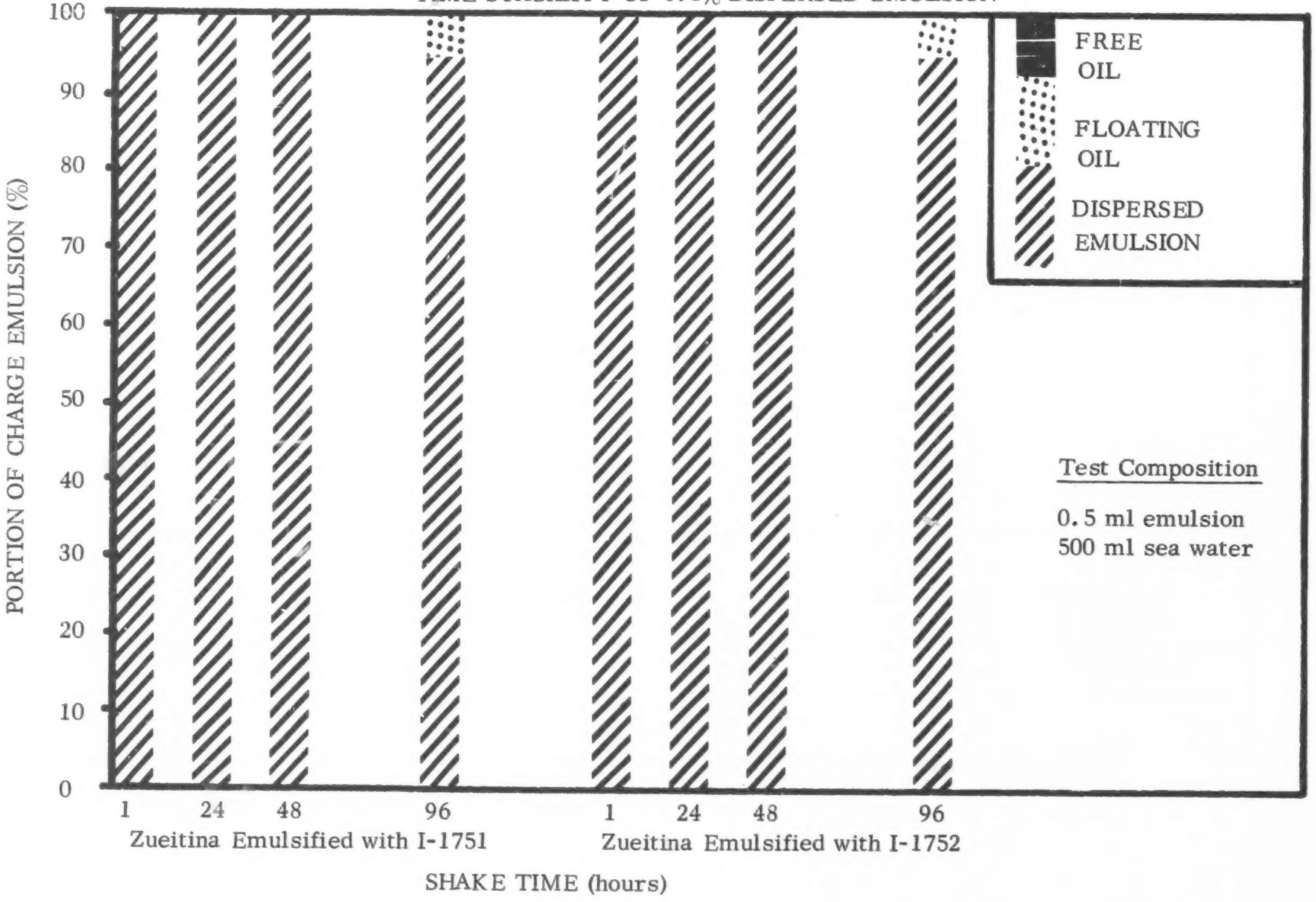


FIGURE 4.4-5
TIME STABILITY OF 0.1% DISPERSED EMULSION

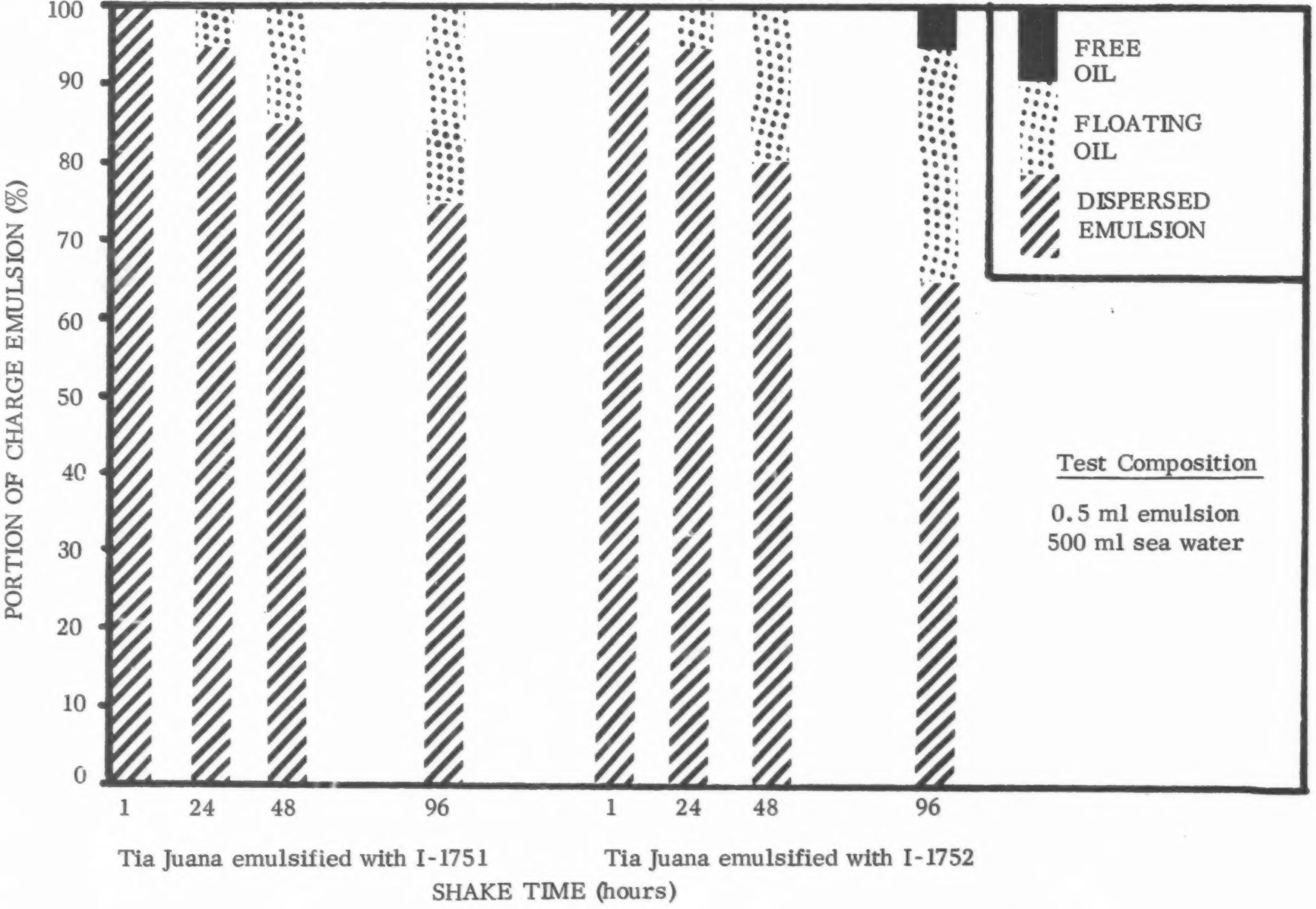
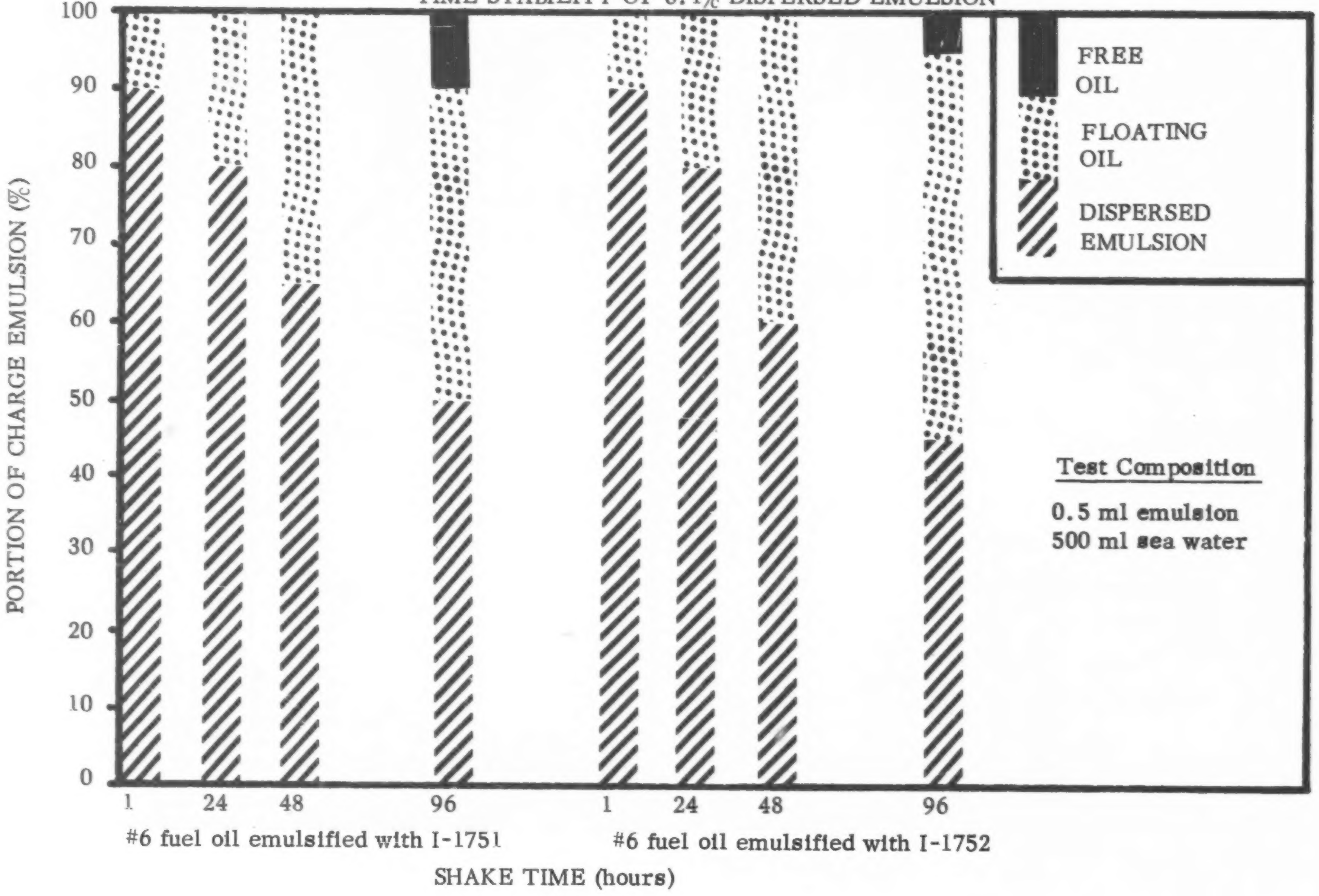


FIGURE 4.4-6
TIME STABILITY OF 0.1% DISPERSED EMULSION



4.5.1 Method

The contractor's concept of the factors involved in the evaporation of these emulsions is described as follows:

1. Encapsulating water jacket loses water and ruptures.
2. Free oil thus released loses light fractions.
3. Protective layer of heavy fractions forms.
4. Cycle of rupture and loss of material repeats at a reduced rate.

Under closed conditions, the vapor phase above the emulsion would reach a state of equilibrium with the liquid phase. In this study, losses of material from various vented systems would be more representative of conditions expected, therefore, the following procedure was selected.

To measure evaporation loss, an amount of emulsion was placed in a 3.8 inch diameter petri dish (61 cm^2 surface area) 1/2 inch in height and weighed. Periodic weighings were recorded to determine weight loss. Determinations were obtained for the following three sets of conditions:

1. A full open dish.
2. A half filled open dish.
3. A half filled dish covered with 1/4 inch vented cover.

The dishes were weighed on two analytical balances (Figure 4.5-1).

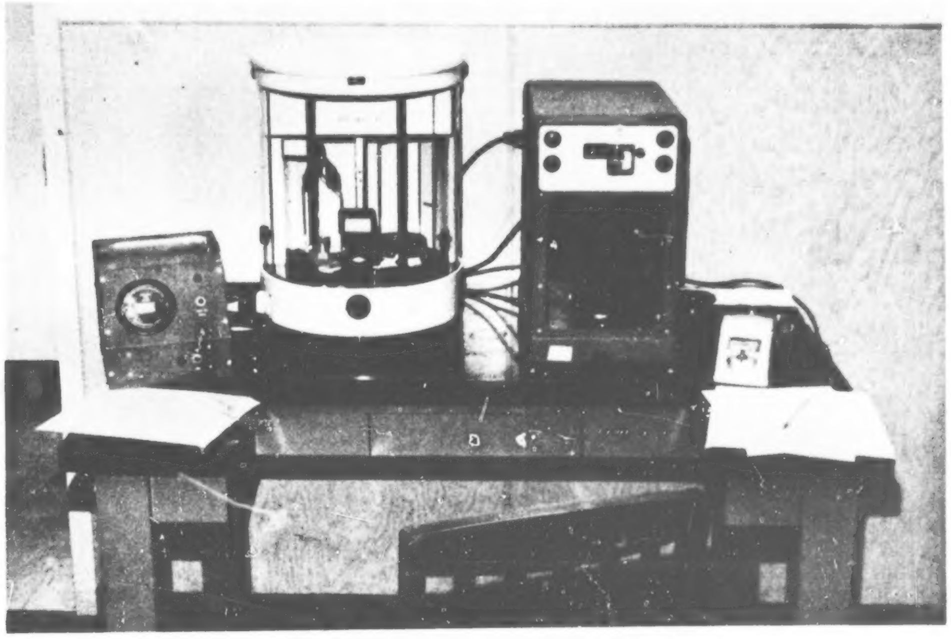


Figure 4.5-1 Analytical Balances with Petri Dishes being Weighed

FIGURE 4.5-2
ACCUMULATIVE WEIGHT LOSS
ZUEITINA CRUDE OIL & EMULSION

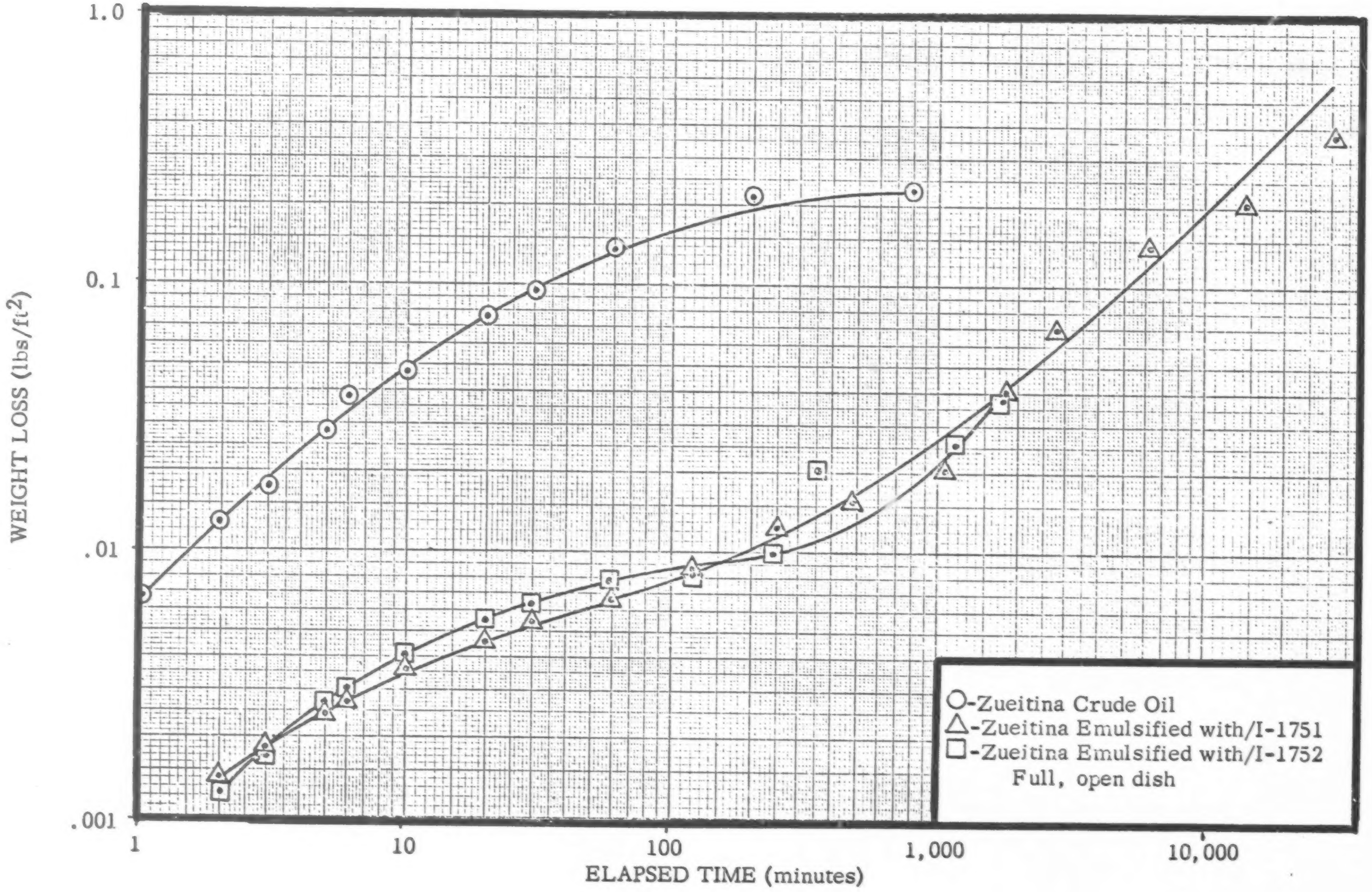


FIGURE 4.5-3
EVAPORATION RATE
ZUEITINA CRUDE OIL & EMULSION

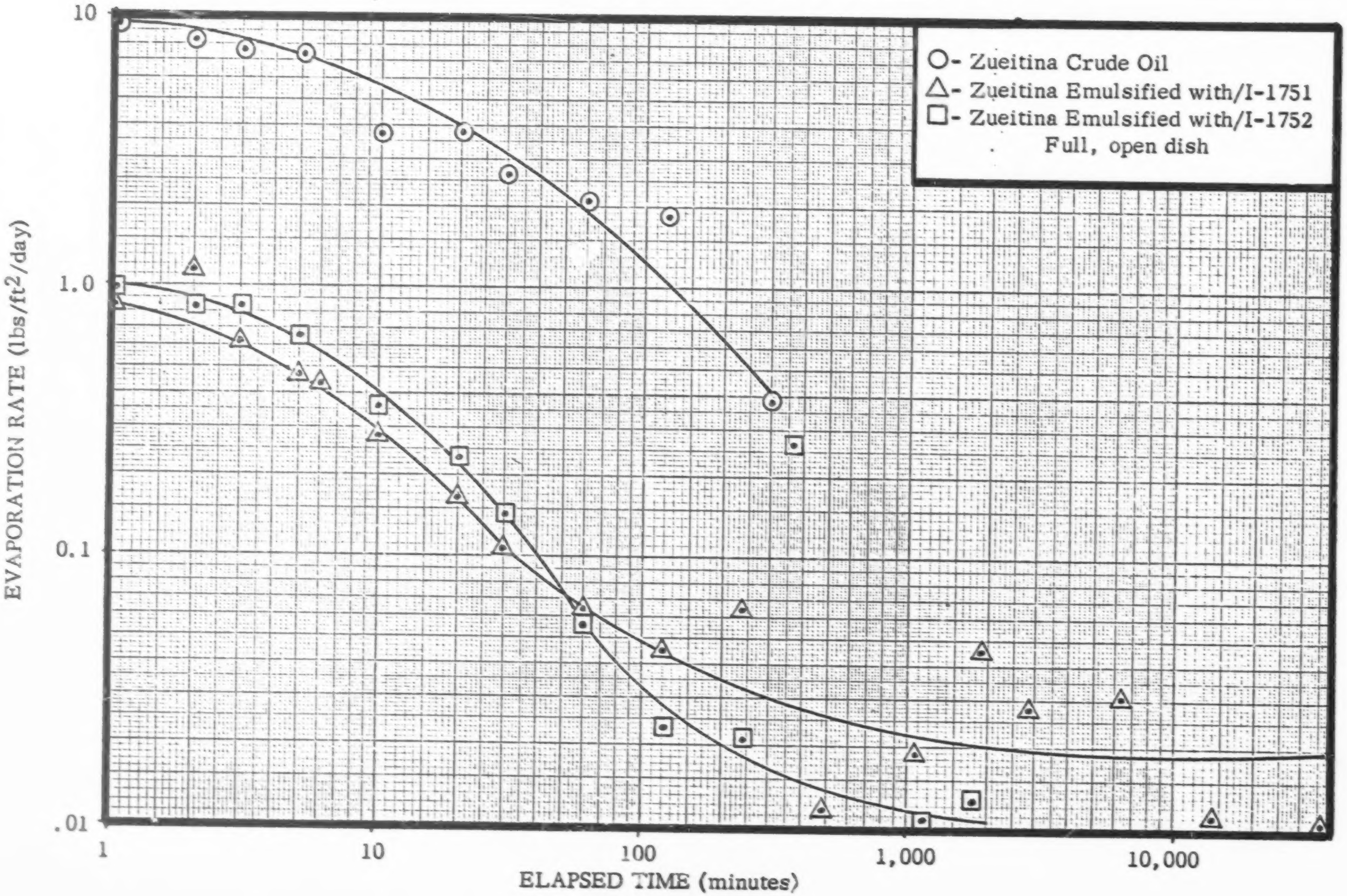


FIGURE 4.5-4
ACCUMULATIVE WEIGHT LOSS
#6 FUEL OIL & EMULSION

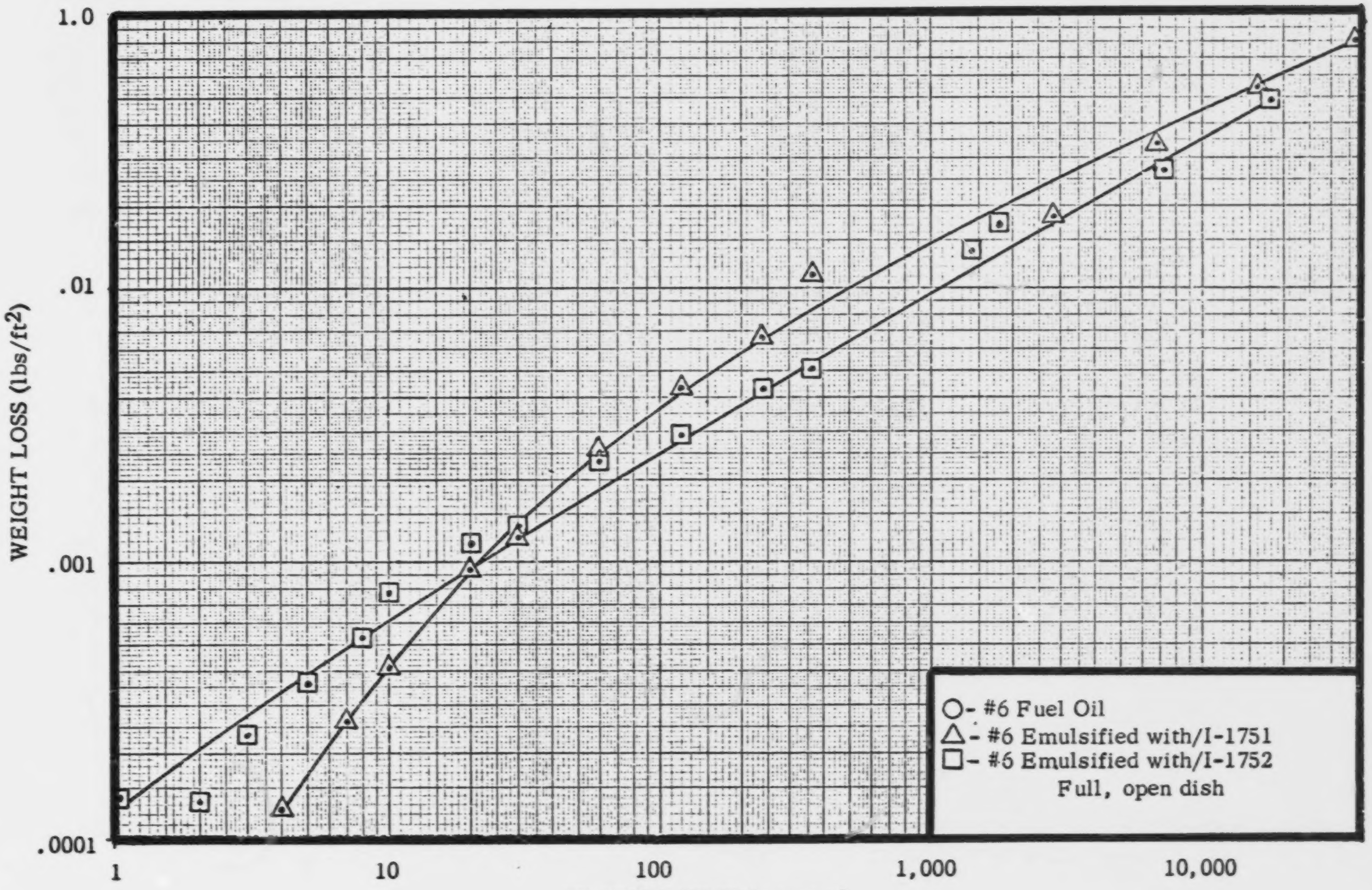


FIGURE 4.5-5
EVAPORATION RATE
#6 FUEL OIL & EMULSION

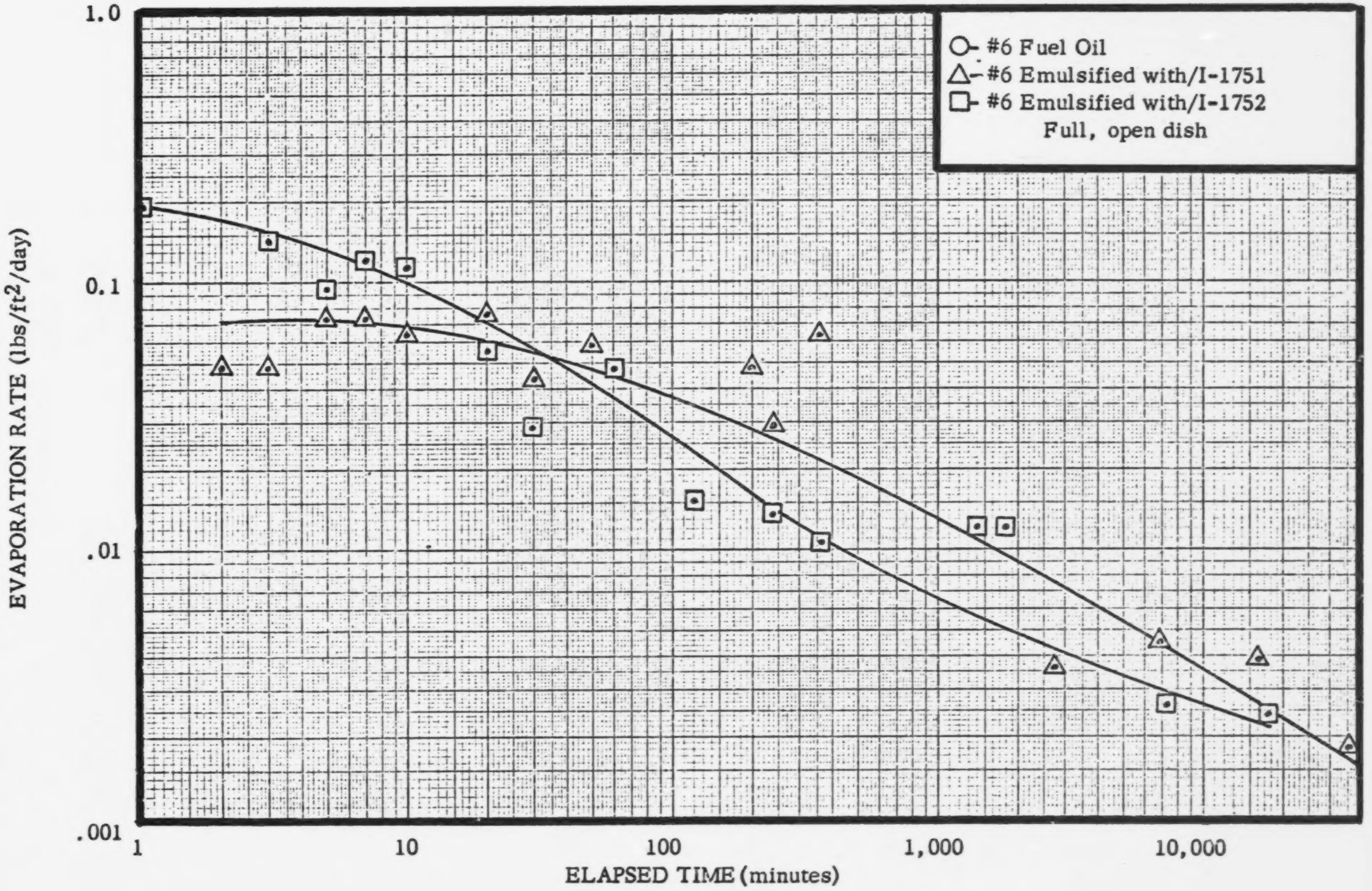


FIGURE 4.5-6
ACCUMULATIVE WEIGHT LOSS
ZUEITINA CRUDE OIL & EMULSION

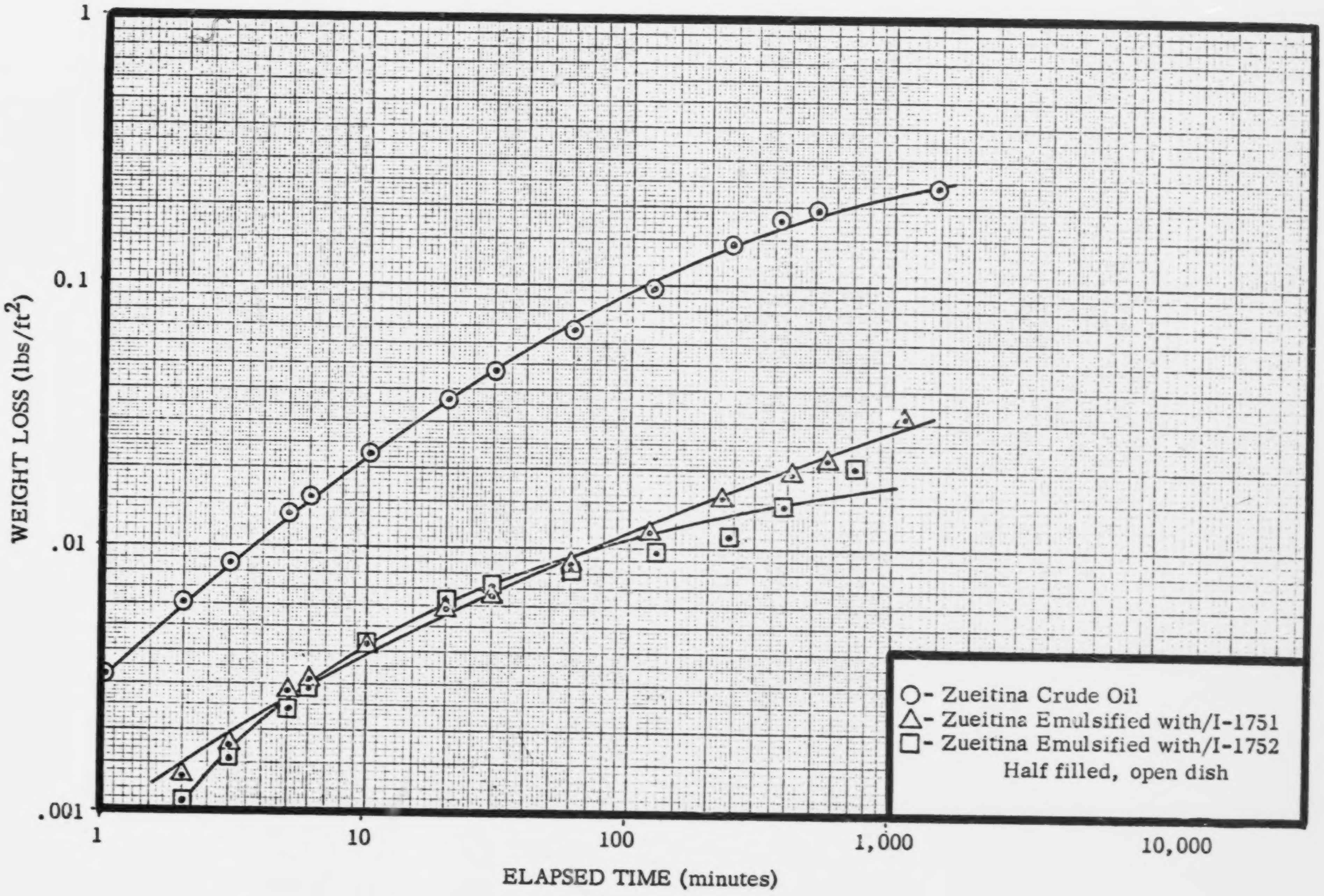


FIGURE 4.5-7
EVAPORATION RATE
ZUEITINA CRUDE OIL & EMULSION

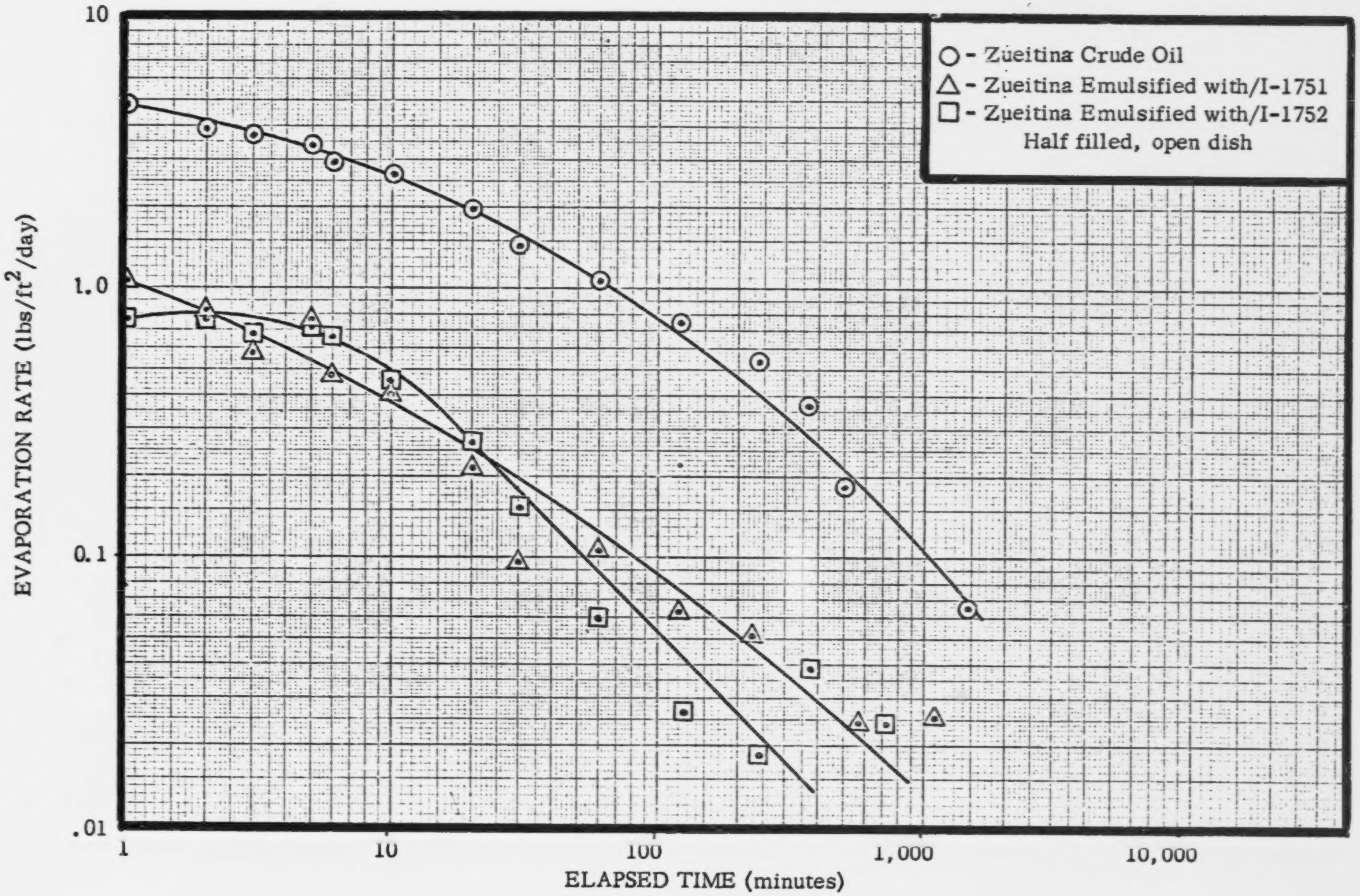


FIGURE 4.5-8
ACCUMULATIVE WEIGHT LOSS
TIA JUANA CRUDE OIL & EMULSION

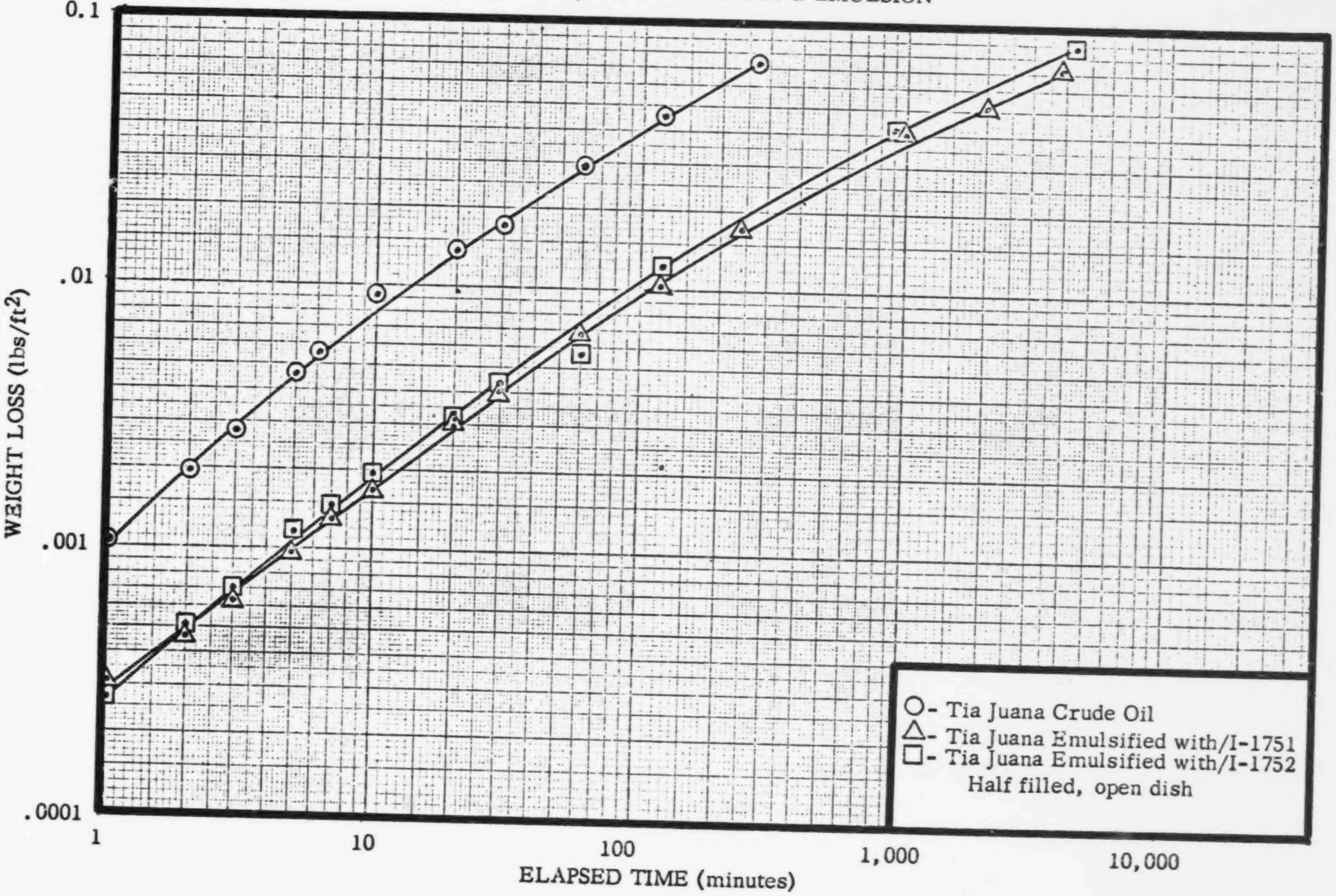


FIGURE 4.5-9
EVAPORATION RATE
TIA JUANA CRUDE OIL & EMULSION

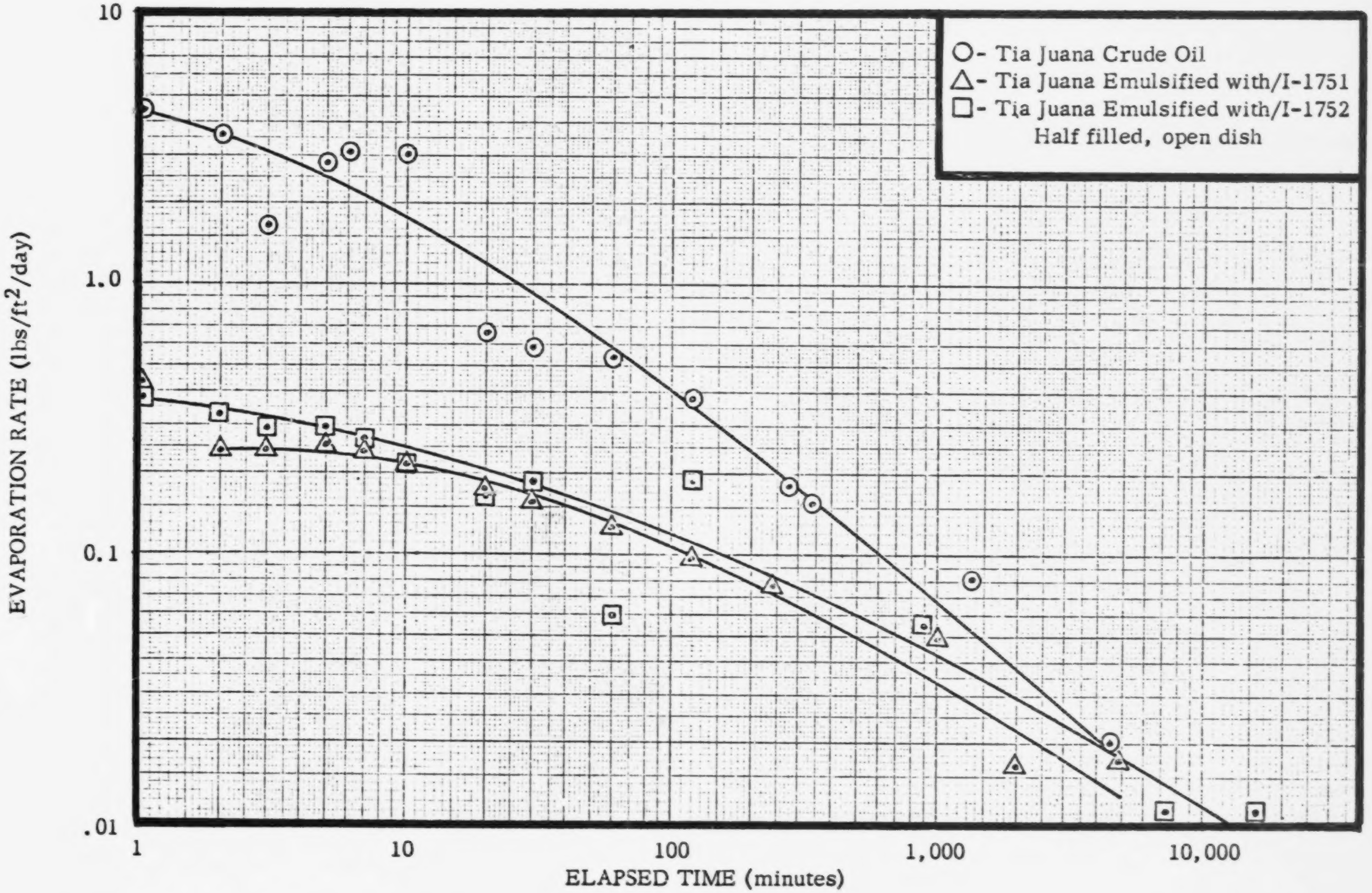


FIGURE 4.5-10
ACCUMULATIVE WEIGHT LOSS
#6 FUEL OIL & EMULSION

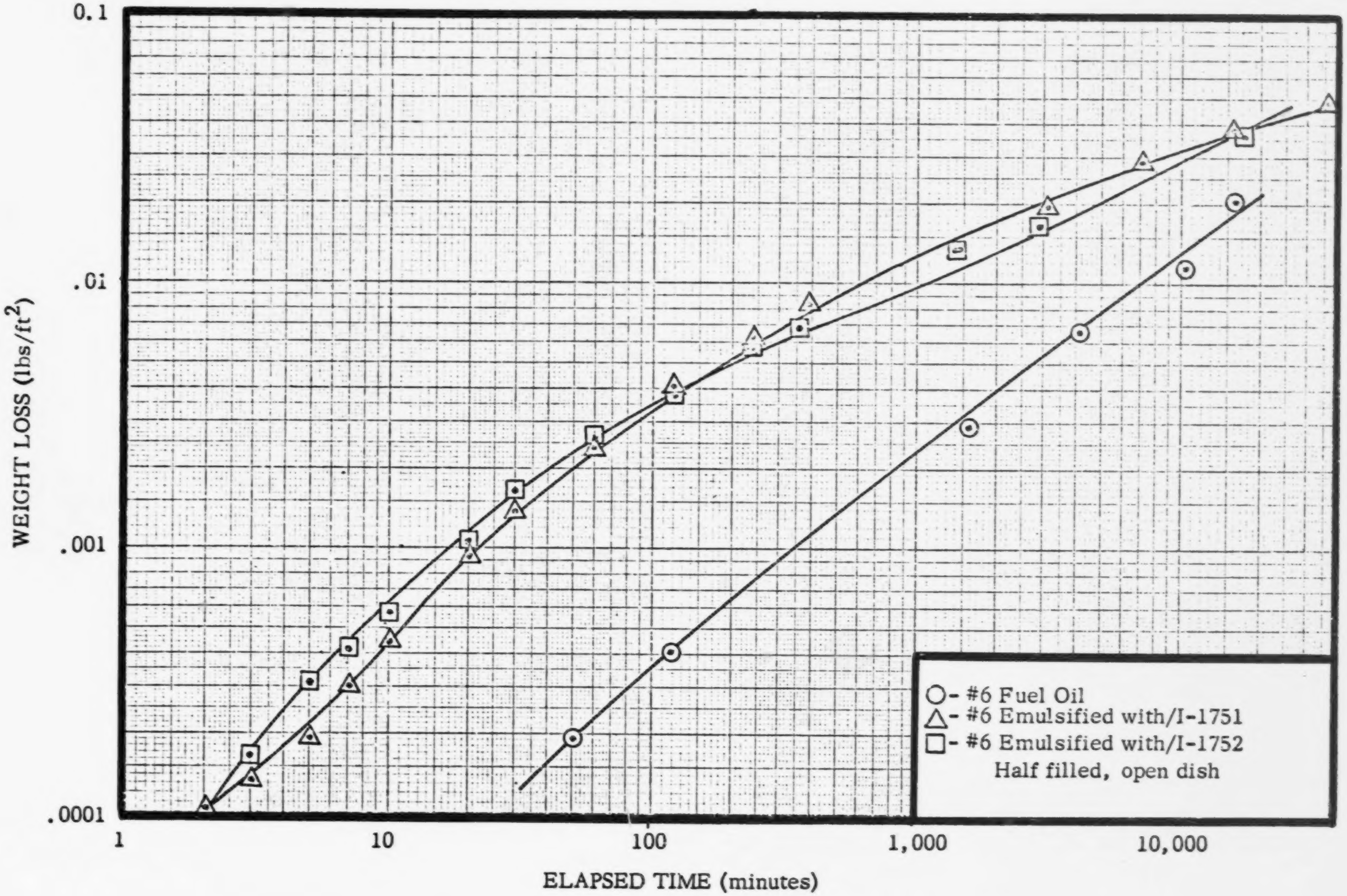


FIGURE 4.5-11
EVAPORATION RATE
#6 FUEL OIL & EMULSION

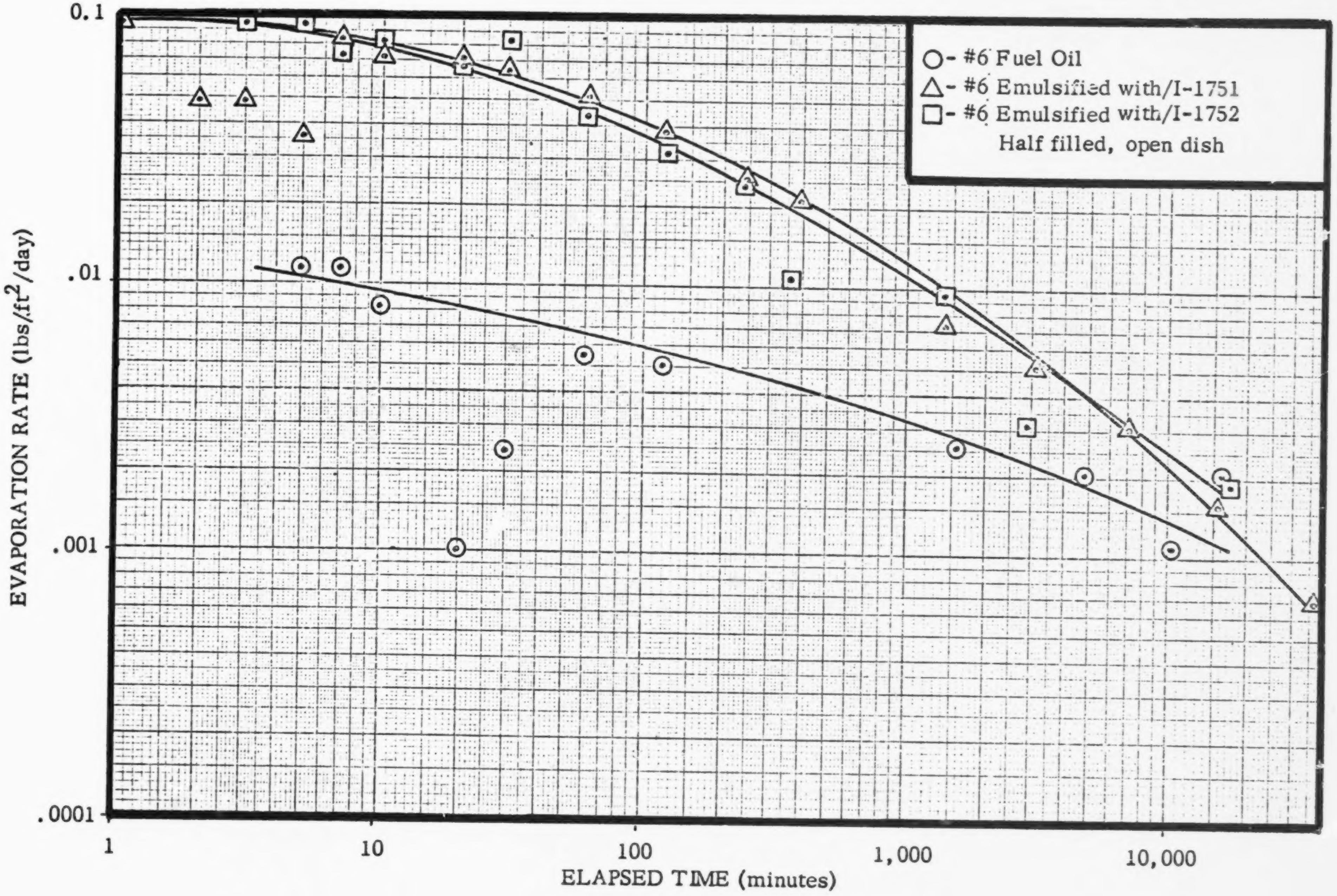


FIGURE 4.5-12
ACCUMULATIVE WEIGHT LOSS
ZUEITINA CRUDE OIL & EMULSION

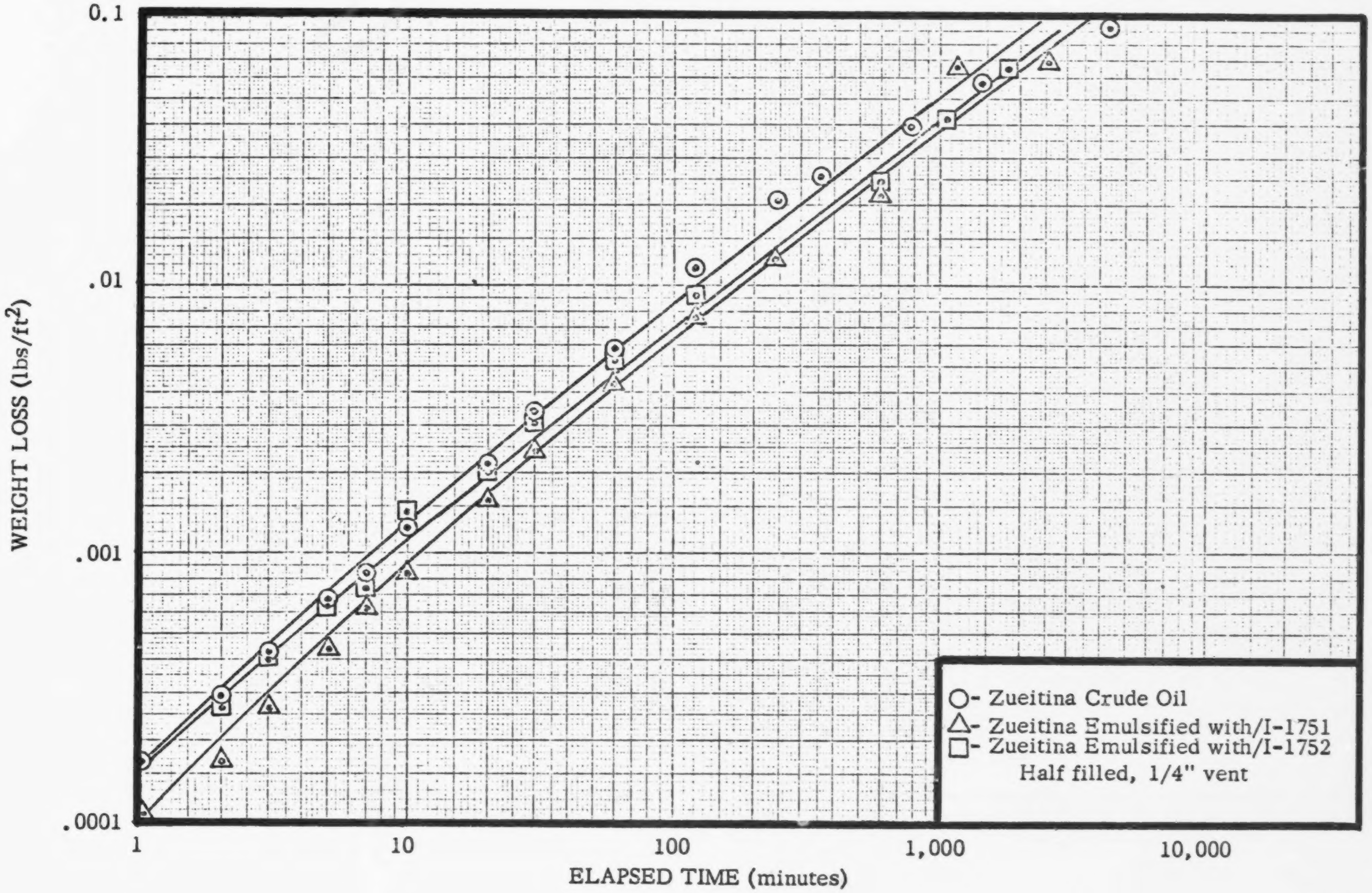


FIGURE 4.5-13
EVAPORATION RATE
ZUEITINA CRUDE OIL & EMULSION

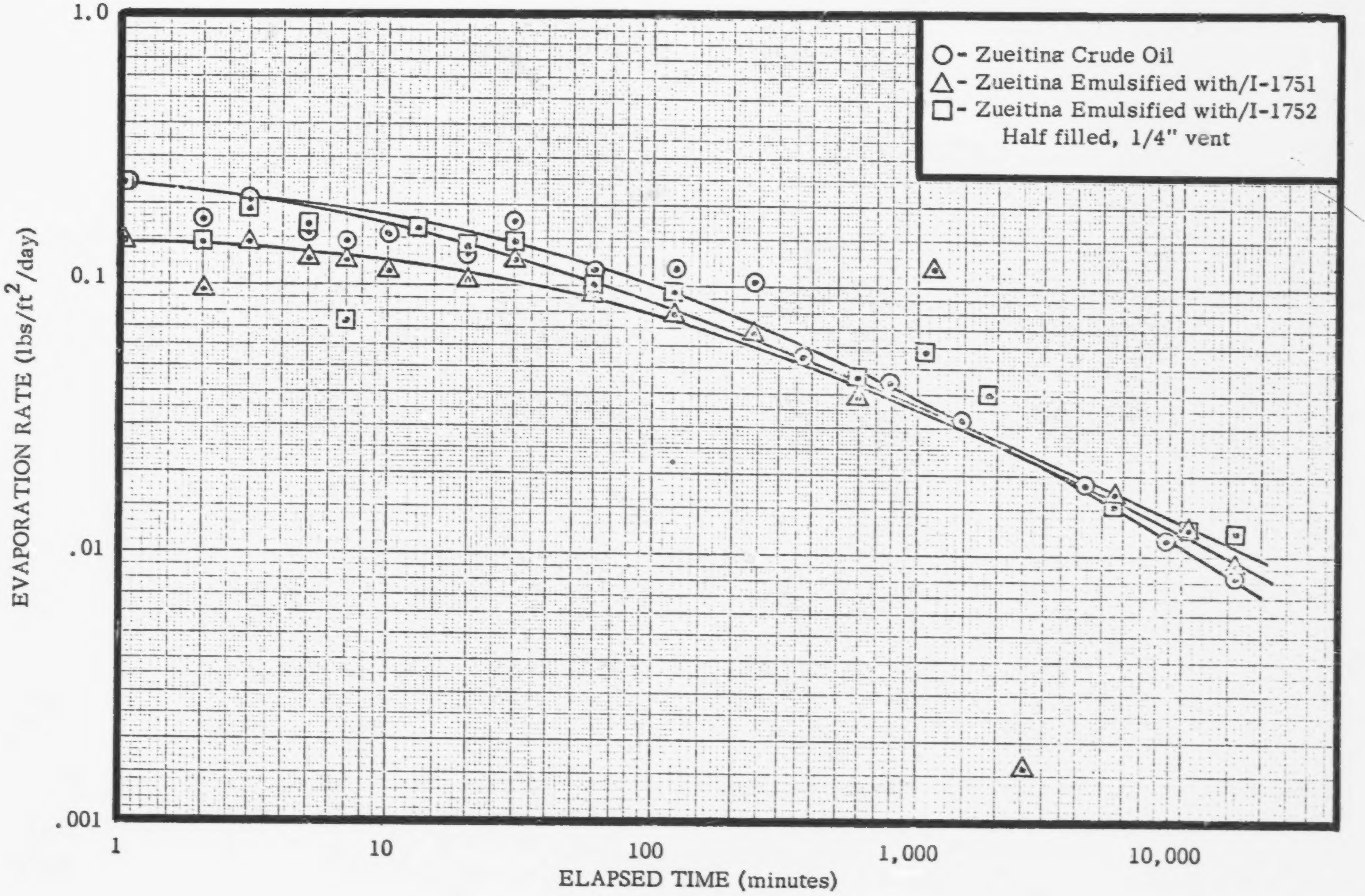


FIGURE 4.5-14
ACCUMULATIVE WEIGHT LOSS
TIA JUANA CRUDE OIL & EMULSION

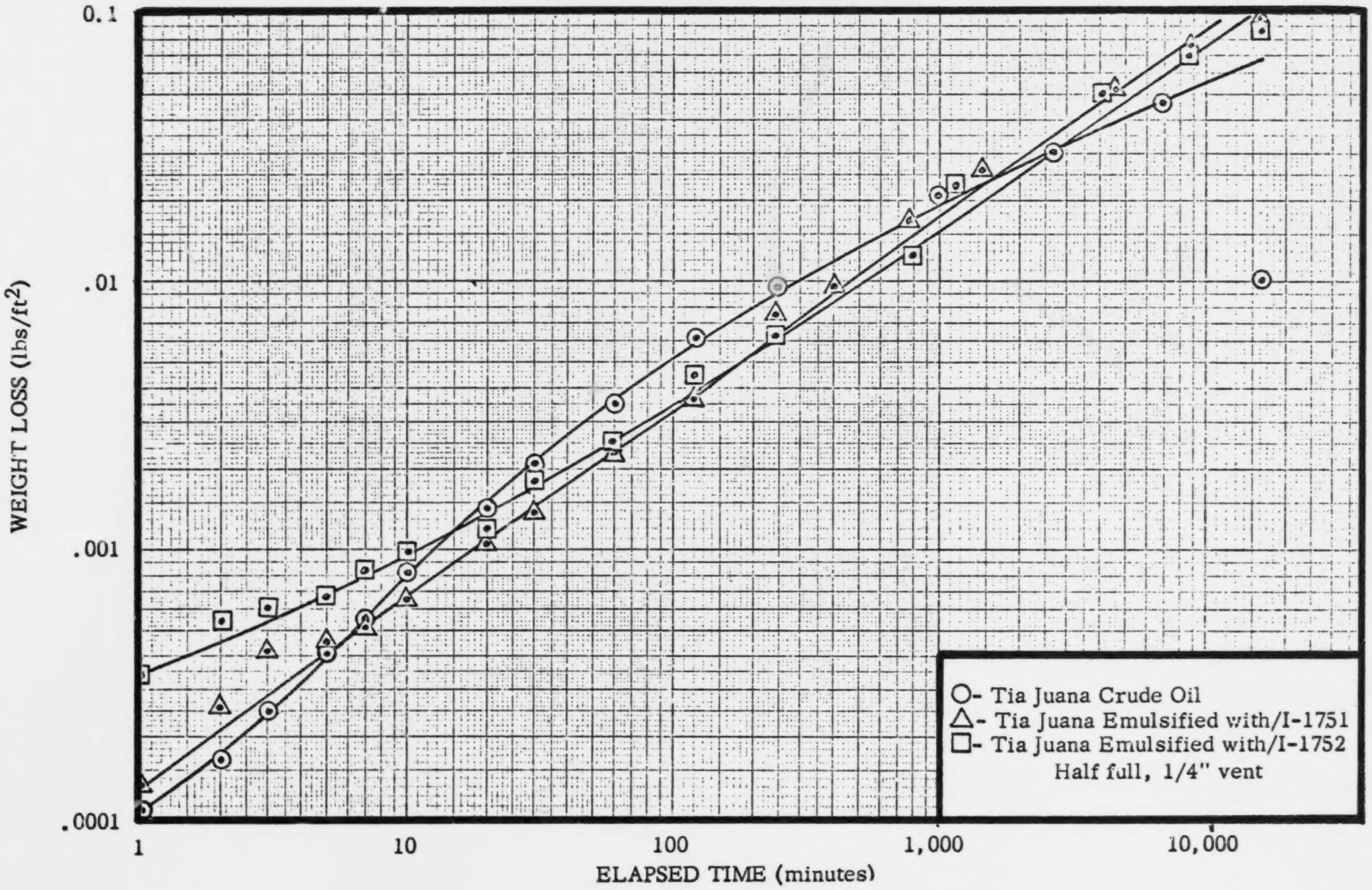


FIGURE 4.5-15
EVAPORATION RATE
TIA JUANA CRUDE OIL & EMULSION

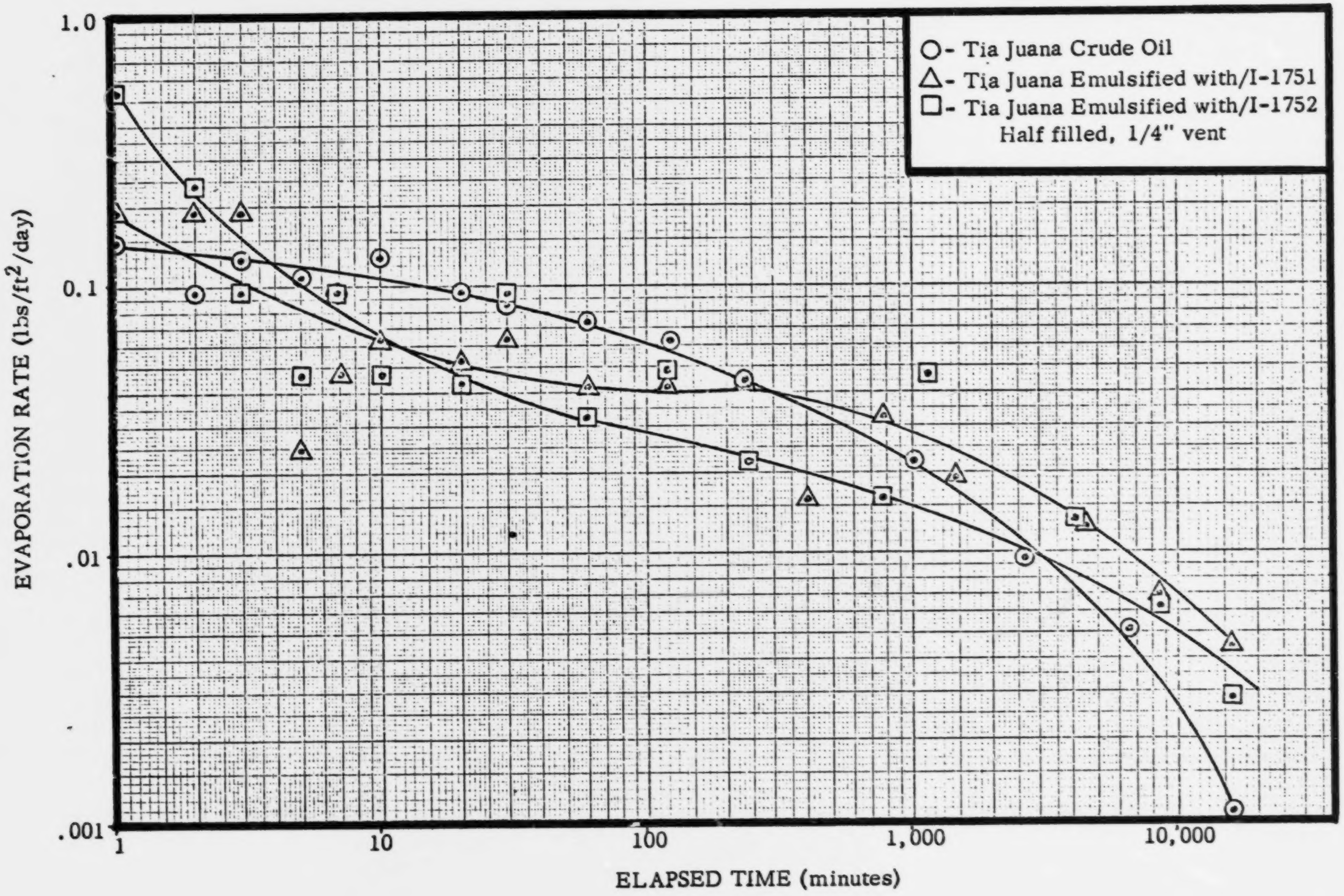


FIGURE 4.5-16
ACCUMULATIVE WEIGHT LOSS
#6 FUEL OIL & EMULSION

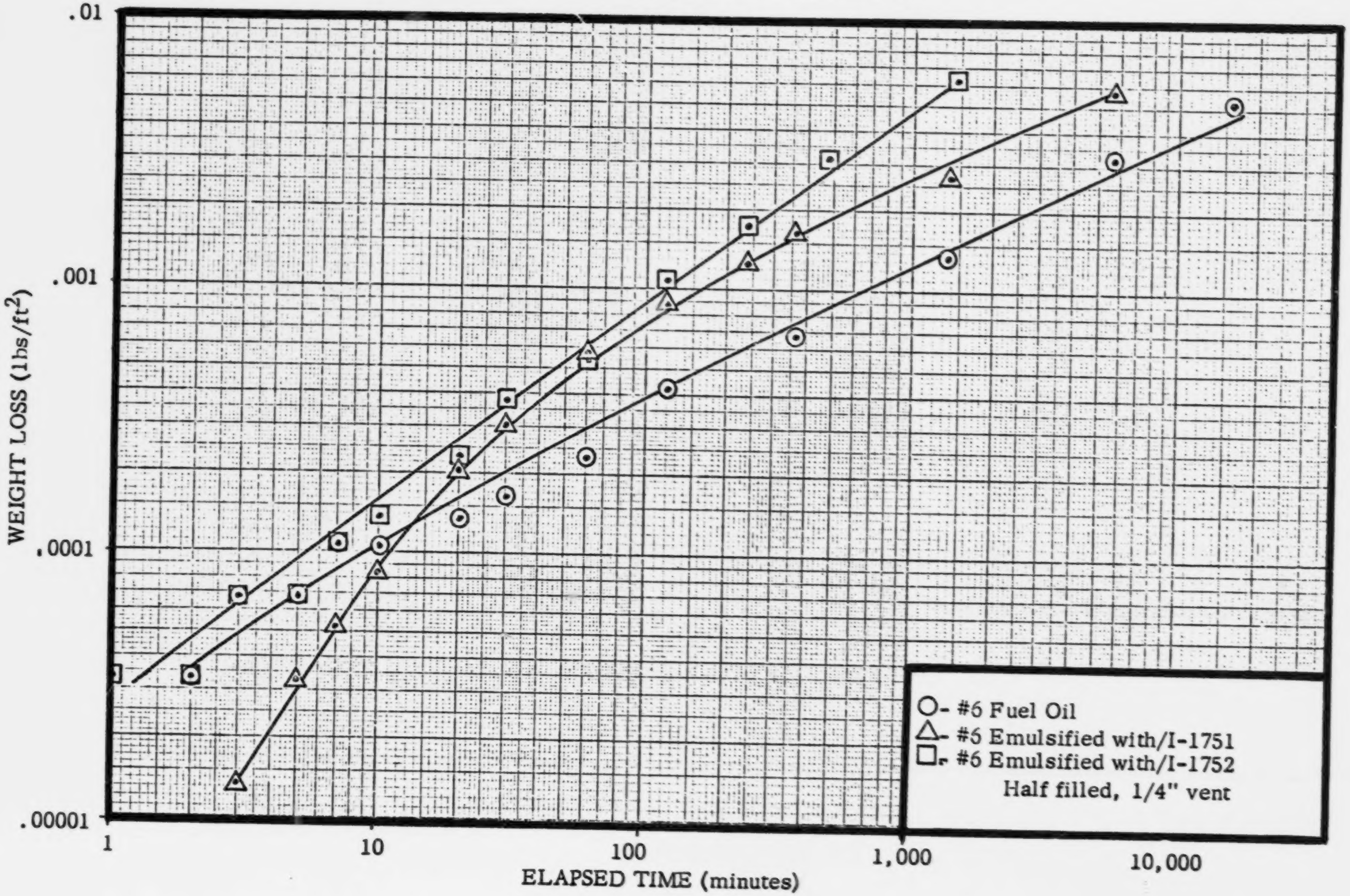
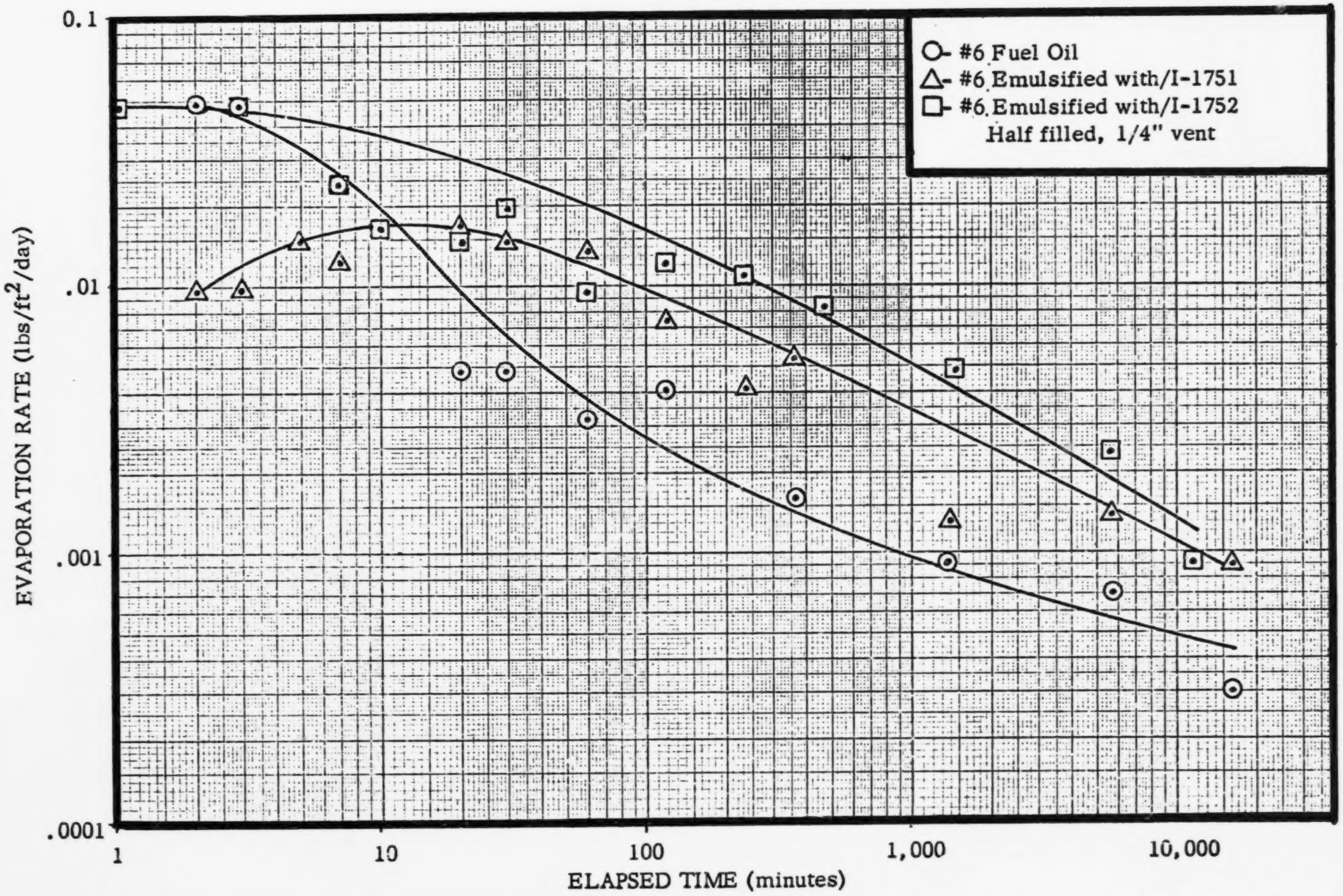


FIGURE 4.5-17
EVAPORATION RATE
#6 FUEL OIL & EMULSION



4.5.2 Evaporation Rate Data

All data are presented in Tables I-1 through I-27 (Appendix I). Data for conditions of "full, open dish" are shown on Figures 4.5-2 through 4.5-5. Data for conditions of "half filled, open dish" are shown on Figures 4.5-6 through 4.5-11. Data for "half filled, 1/4 inch vented cover" are shown on Figures 4.5-12 through 4.5-17.

4.5.3 Discussion of Evaporation Rates

The filled, open dish, evaporation rate data (presented graphically in Figures 4.5-2 through 4.5-5) show that evaporation of the Zueitina crude oil is reduced by a factor of 10 when the oil is emulsified. The half filled, open dish data (Figures 4.5-6 through 4.5-11) show a reduction factor of 5 for the Zueitina emulsions compared to the free oil. The difference between the filled dish and the half filled dish is accountable to the evaporation rate of the free oil. The emulsions, whether in a filled or half filled dish, evaporated at about the same rate. However, the free oil evaporated from the half filled dish at half its rate of evaporation from the filled dish. The half filled, open dish of Tia Juana medium emulsions had an initial evaporation rate one-tenth that of the free crude oil. Within one hour of exposure to the atmosphere the evaporation rate of the free oil was only five times as great as that of the emulsions.

The #6 Fuel Oil emulsions showed a reversal of trend. The free oil initially evaporated at a rate approximately one-tenth that of the emulsions. This reversal may, in part, be explained by the extremely low vapor pressure of the #6 Fuel Oil. The vapor pressure of the #6 Fuel Oil at 100° F was less than the vapor pressure of water under the same conditions.

The rate of evaporation in the vented dish was quite different than in the open dish. In the half filled one fourth inch vent covered dish evaporation rate tests, data (Figures 4.5-12 through 4.5-17) indicate a rate of evaporation for the emulsions which is comparable to the rate for the free oil. This was the case for all three oils and the emulsions. For the Zueitina crude and emulsion, the evaporation rate for both emulsions and the free oil was approximately one-tenth the rate of the open dish emulsions. The evaporation rate of free oil and emulsions in the vented dish was approximately one one hundredth the evaporation rate of the free oil in the open dish.

The vented dish evaporation rate tests indicate that no significant reduction in cargo evaporation loss can be expected as a result of emulsification. However, in the event of an exposed spill the evaporation rate would be substantially reduced with a corresponding reduction in hazard to sea craft in the vicinity of a spill.

Additionally, the ligher fractions of the petroleum would be retained by the emulsion until dispersion had widely separated the oil droplets. The retention of the light fractions would tend to prevent formation of the thick, sticky mass which so often appears a few days after a large oil spill.

4.6 Increased Safety

One major hazard of hydrocarbon transportation is fire. This hazard can be minimized or eliminated by thickening the petroleum crudes or products to be carried. Emulsification is one of the best approaches from both technical and practical standpoints for thickening such materials. Laboratory tests have been developed for measuring the characteristics of hydrocarbons that contribute to fire hazards. For this study, two tests were selected: (1) Flash point determination and (2) Vapor pressure determination.

4.6.1 Flash Point Determinations

4.6.1.1 Method

Flash point determinations were performed in accordance with STANDARD METHOD OF TEST FOR FLASH POINT BY MEANS OF THE PENSKY-MARTENS CLOSED TESTER (ASTM designation: D 93). Of two standard accepted methods for flash point determinations, the Pensky-Marten Procedure is used for the less volatile and more viscous petroleum products and is considered superior for flash point determinations of emulsions.

4.6.1.2 Flash Point Data

Comparison of flash point determinations for the various test samples are shown in Table 4.6-1. Included are data for the sample "as received" as well as data for the emulsions (two emulsifiers).

TABLE 4.6-1

COMPARISON-FLASH POINTS
(Pensky-Martens Method)

Crude or Product	As Received (°F)	Emulsifier	Emulsified (°F)	Change (°F)
Zueitina	42	I-1751	84	+ 42
		I-1752	82	+ 40
Tia Juana	64	I-1751	96	+ 32
		I-1752	92	+ 28
#6 Fuel Oil	220	I-1751	240	+ 20
		I-1752	240	+ 20

4.6.2 Vapor Pressure Determinations

4.6.2.1 Method

Reid vapor pressure determinations for this study were performed in accordance with STANDARD METHOD OF TEST FOR VAPOR PRESSURE OF PETROLEUM PRODUCTS (ASTM Designation D 323).

4.6.2.2 Vapor Pressure Data

Comparisons of vapor pressures are shown in Table 4.6-2. Vapor pressures were determined for the samples "as received" as well as the samples in their emulsified form (two emulsifiers).

TABLE 4.6-2

COMPARISON-VAPOR PRESSURES
(Reid Method)

Pressure at 100° F

Crude or Product	As Received (psia)	Emulsifier	Emulsified (psia)	Change (%)
Zueitina	8.2	I-1751	4.2	-49
		I-1752	4.8	-41
Tia Juana	4.2	I-1751	2.1	-50
		I-1752	2.3	-45
#6 Fuel Oil	0.4	I-1751	0.1	-75
		I-1752	0.1	-75

4.6.3 Rupture Leakage Tests

4.6.3.1 Method

Yield value is a standard test to measure the reluctance of emulsion type material to flow through holes or ruptures. Viscosity is typically used to compare flow characteristics of Newtonian fluids. In this study, yield values were determined by the modified ASTM D 217 method and viscosities were measured by ASTM D 445 (Ostwald modification).

In addition, qualitative tests to determine rates of water influx from the sea environment and spill rate to the atmosphere were performed. Procedures for these tests were as follows:

Water Influx - consisted of puncturing a 2 7/8 inch diameter by 5 inch high can with a chisel to form a 1 inch by 1/4 inch rupture, 1/8 inch from the bottom of the can. The can was filled to a 4 inch level with 500 ml of emulsion or oil and placed in a fish acclimatizing tank filled with 20° C (68° F) synthetic sea water. Water agitation was created by intermittent hand stirring with an 8 inch square board in a plunger motion, up and down, to create waves. After two hours in the tank, the rupture was covered, the can removed and the influxed sea water drained into a graduated cylinder and the amount of water measured.

Spill rate - used the same ruptured can as described above. The spillage rate was recorded in ml/sec as the material was allowed to drain from the container, filled to a liquid level of 4 inches, into a graduated cylinder under atmospheric conditions.

4.6.3.2 Rupture Leakage Data

Table 4.6-3 gives the flow properties of the oils and emulsions as indicated by viscosity and yield values. Table 4.6-4 presents the influx of sea water tests results and Table 4.6-5 gives the spill rate of the oils and emulsions.

TABLE 4.6-3

OIL AND EMULSION FLOW PROPERTIES

Crude or Product	As Received Viscosity (cp)	Emulsified Emulsifier	Emulsified Yield Value (dynes/cm^2)
Zueitina	3.4	I-1751	600
		I-1752	500
Tia Juana	26.0	I-1751	600
		I-1752	550
#6 Fuel Oil	2490	I-1751	1800
		I-1752	1550

TABLE 4.6-4

RUPTURE TESTS-INFLUX OF SEA WATER

Crude or Product	As Received (ml)	Emulsified Emulsifier	Emulsified Influx (ml)
Zueitina	109	I-1751	15
		I-1752	21
Tia Juana	101	I-1751	16
		I-1752	17
#6 Fuel Oil	64	I-1751	0.5
		I-1752	1.0

TABLE 4.6-5

RUPTURE TESTS-SPILL RATE

Crude or Product	As Received (ml/sec)	Emulsified Emulsifier	Emulsified Spill (ml/sec)
Zueitina	230	I-1751	0.5
		I-1752	0.4
Tia Juana	170	I-1751	0.4
		I-1752	0.4
#6 Fuel Oil	0.8	I-1751	0.0
		I-1752	0.0

4.6.4 Discussion of Increased Safety

Problems of safety in transportation of petroleum crudes and products closely parallel the problems of handling fuels. Considerable work has been done in this field to change characteristics of fuels to improve safety. Emulsification of fuels leads most other developments in this problem area as a possible solution.

The relative flammability of various materials is typically used to measure the danger involved. Rates of vaporization, flash points, and time required for materials to begin to burn are considerations in determining relative flammability. Emulsions reduce the rate at which combustible vapors are released from the hydrocarbon phase. The two laboratory tests selected to measure improvements in reduction of flammability for this study were flash point and vapor pressure.

The flash point of a material is determined through the exposure of the material to a flame under controlled conditions. The flash point is recorded as the temperature read on a thermometer submerged in the test material at the time the flame application causes a distinct flash in a measuring cup. Flash points are compared in Table 4.6-1. It can be seen that the high gravity Zueitina crude has a much lower flash point than the Tia Juana Medium gravity crude which in turn is substantially less than the #6 Fuel Oil. Increases in flash point represent improved conditions from the standpoint of safety. The necessity for improvement is much greater for low flash point petroleum crudes which represent a much more hazardous material to transport.

Vapor pressure is a measure of the tendency of a liquid to vaporize. Explosions of vapors, caused by the vaporization of hydrocarbon materials, is one of the hazards in transporting and handling hydrocarbon materials. Rates of vaporization represent a second approach to determining the relative flammability of various materials. A comparison of vapor pressures for the various test materials is shown in Table 4.6-2. Substantial reductions in vapor pressure were achieved through the emulsified forms for all of the test samples used in this study. This is contrary to what would be expected thermodynamically for the vapor pressure of two immiscible phases in equillibrium. It must be concluded that the emulsions lost vapor so slowly that equillibrium was not obtained during the Reid vapor test. These results are in agreement with published data on the Reid vapor pressure of fuel emulsions.

Flow properties of emulsions differ greatly from those of the raw forms of the material itself. Emulsions of the type prepared and tested in this study can be moved through conventional piping, yet will resist flow out of a hole or rupture in a containing vessel. A comparison of apparent viscosity for the raw material with penetrometer yield values for the emulsified form is shown in Table 4.6-3. Results are typical for emulsions prepared with the type emulsifiers used in this study. Emulsions with stiffer textures can be obtained with different emulsifiers; however, emulsifier optimums were beyond the scope of the present study.

There are numerous other considerations and laboratory tests, not performed in this study, to measure improvement in safety of emulsified liquid hydrocarbons compared to the free oil. Burning rate is often considered. Emulsions will always start to burn at a slower rate, and this additional short time available at the start of a catastrophe often permits control. Flame propagation is another consideration in determining relative flammability. This test measures the speed at which flame moves along a path under controlled conditions. Flame propagation times are substantially increased for hydrocarbon liquids in emulsified form, thus again allowing additional time at a critical point. Formation of ignitable mixtures on impact of vessels is also severly slowed for emulsified combustible liquids as compared with free oils.

In loading and unloading liquid hydrocarbons, static charge build-up is an always potentially serious hazard. Emulsions are so much more conductive than free oils that the static hazard becomes negligible.

Fire hazards aboard vessels at sea and at docks are serious problems. A recent Associated Press news release points up the frequency of such fires. Within a two week period, three of the world's largest ships suffered explosions and fire. These were the Norwegian-King Haakon VII - 220,000 tons, the British Mactra- 205,000 tons, and the British Marpessa - 207,000 tons.

Emulsification significantly improves the safety of transporting and handling liquid hydrocarbons. Such an improvement should result in substantial reduction of insurance rates.

4.7 Toxicity

4.7.1 Method

The procedure used in this study was one furnished in draft form by the Federal Water Pollution Control Administration, dated Novemver 18, 1968. The method was provided only as an "interim guide" to be used until standard procedures had been developed and endorsed by Federal Water Pollution Control Administration (FWPCA). The procedure is a comparative bioassay performed in accordance with the procedure contained in Standard Methods for the Examination of Water and Waste Water, 12th Edition, modified to insure the comparability of the data from different test laboratories.

4.7.2 Test Apparatus

A specially insulated test laboratory was constructed with a thermostatically controlled air conditioning system to maintain the required temperature control. Two fifty gallon glass tanks were used for acclimatizing the test specimens (Figure 4.7-1). Both were located in the test laboratory to assure the required constant temperature conditions for acclimatization.

Fish were exposed to the test emulsions and emulsifiers in five gallon glass test aquaria (Figure 4.7-2). One gallon fish bowls were used for the exploratory tests to determine the ranges of treating concentrations for the actual test determinations.

Requirements for liquid re-aeration were limited to the acclimatizing tanks. Aeration was achieved through constantly supplied compressed air filtered through a five micron cartridge filter followed by a 0.5 micron membrane filter.

The proper level of agitation in the test containers was provided by a bank of magnetic stirring bars. All magnets were rotated by pulleys driven by the same electrical drive motor and gear box, thus assuring the same rate of agitation in each test container.

4.7.3 Test Fish and Experimental Water

Fish selected for this salt water test were Cyprinodon variegatus (Figure 4.7-3). This species is one of those acceptable for the Gulf Coast salt water environmental studies. All test fish were obtained from a single location near Houston, Texas. Size of the fish varied from 1 3/4 inches to 2 3/4 inches in length with an average of approximately 2 1/4 inches. All test specimens used in the toxicity determinations met the criteria for fitness. Less than 10 percent died during the four day period prior to the start of tests.

A standard water was used in order that tests results would be comparable as instructed in the FWPCA's "interim guide" for toxicity determinations. Standard sea water was prepared by dissolving "packaged sea salts" in demineralized water free of any metal ions. An analysis of the test water is shown on Table 4.7-1 of this report. The pH of test water was adjusted in each case to 8.0 and controlled to a level not less than 7.8 during the test.

4.7.4 Test Conditions

The test laboratory temperature was 20° ± 1° C and was controlled precisely with a thermostatically controlled air conditioning system. All acclimatizing vessels and test containers were located in this laboratory.

Depth of liquid in test containers was nine inches.

Dissolved oxygen content was monitored daily throughout the tests. It ranged from 5 mg/l to 7 mg/l at all times. Re-aeration of liquid was not required in the test containers.

In each actual toxicity test, ten fish were exposed to the test material. Gentle agitation was provided in the test containers with magnetic stirring bars. Throughout all tests the rotational speed of the stirring bars was held constant at 210 rpm.

4.7.5 Procedure

Five exploratory tests were performed prior to each actual test to determine the proper range of concentrations to be covered in the full scale tests. Results

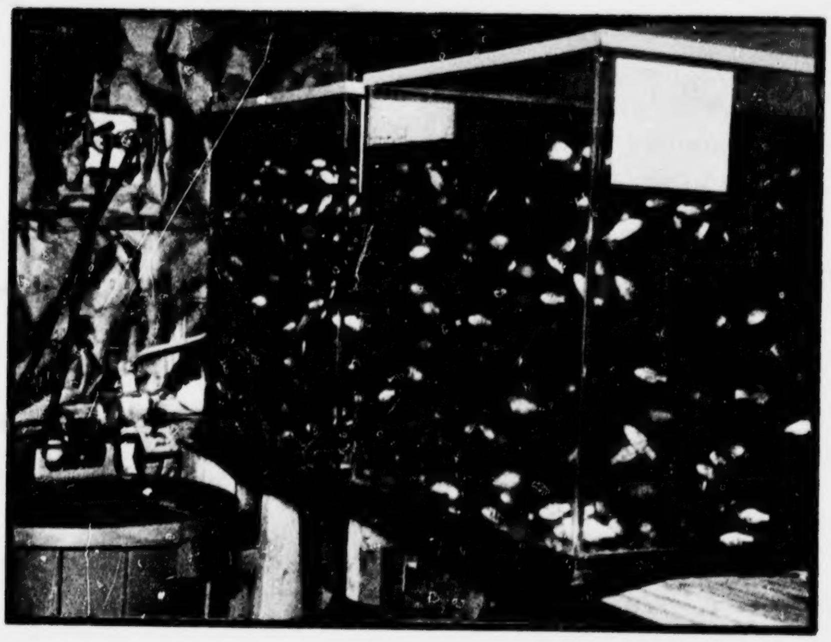


Figure 4.7-1
Acclimatizing Aquaria

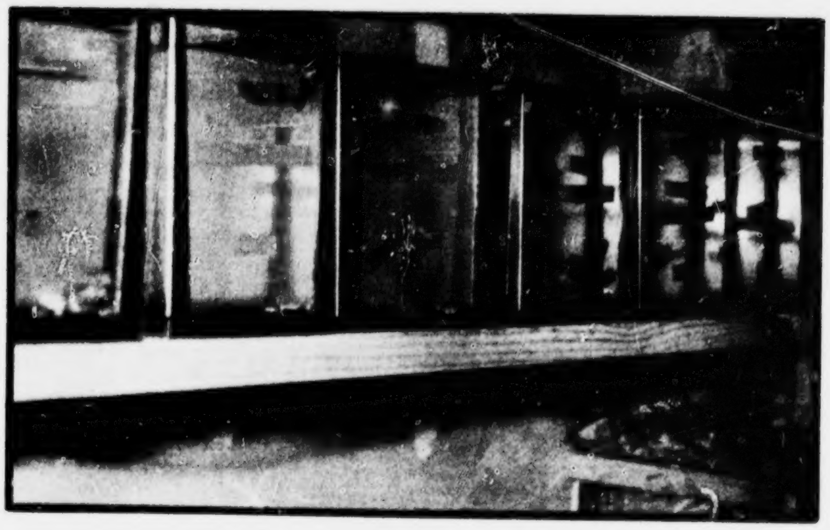


Figure 4.7-2
Toxicity Test Aquaria

Figure 4.7-3
Test Fish --
Cyprinodon variegatus

Table 4.7-1

Analysis of Synthetic Sea Water

Client Federal Water Pollution Control Administration - Department of the Interior

County **State**

Field **Lease** **Well No.**

Formation **Depth** **Perf.**

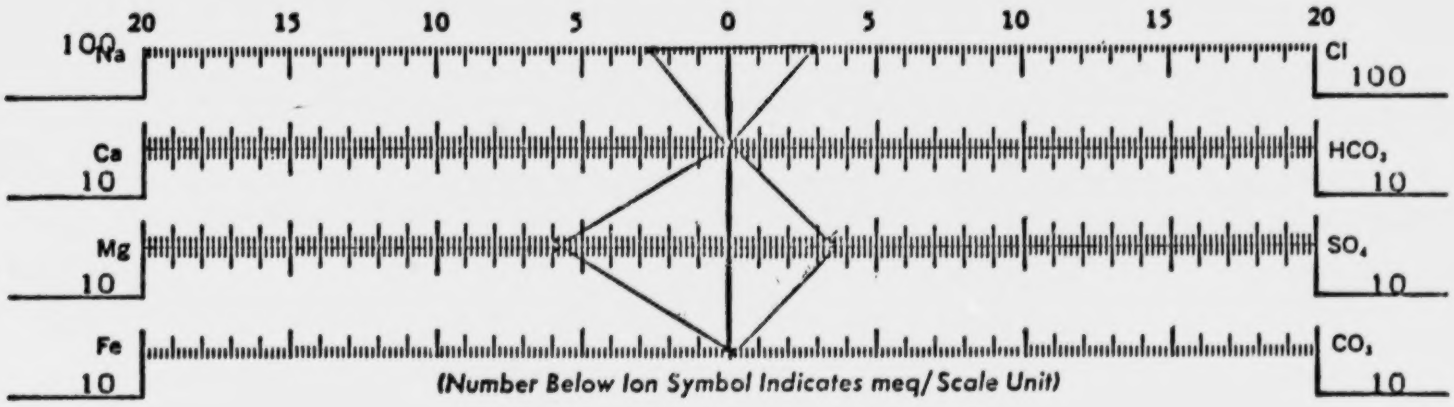
Source of Sample Contract No. 14-12-559

Date Collected Rec: 7-21-69 **by**

REPORT OF WATER ANALYSIS

Lab. Number	P-538	**Specific Gravity**	1.014	**pH**	8.9
Total Dissolved Solids	19113	**Resistivity (Ohmmeters at 68° F.)**	0.0360	**Hydrogen Sulfide**	ABSENT

DISSOLVED MINERAL ANALYSIS PATTERN



(Number Below Ion Symbol Indicates meq/Scale Unit)

DISSOLVED SOLIDS ANALYSIS

	mg/l	meq/l
Total Solids (Calc.)	19113	
Sodium (Calc.)	6180	268.9
Iron (Dissolved)	0	0.0
Barium	-	-
Calcium	35	1.7
Magnesium	722	59.3
Chloride	10400	293.3
Bicarbonate	76	1.2
Carbonate	0	0.0
Sulfate	1700	35.4

PRECIPITATED AND SUSPENDED SOLIDS ANALYSIS

			mg/l
Total Undissolved Solids			
Oil (Solvent Soluble)			
Acid Solubles			
Iron	as		
Calcium	as		
Magnesium	as		
Sulfate	as		
Organic (Ignition Loss)			
Acid Insolubles			
Sand & Clay			
Barium Sulfate	(Quan.)		
	(Qual.)		

TOTAL IRON

SOLUBILITY CALCULATIONS

Calcium Carbonate Stability Index at 77° F ______ Scaling Tendency ______

Calcium Sulfate Stability at 95°F

Concentration ______ meq/l. Calc. Solubility ______ meq/l. Percent Saturation ______

Barium Sulfate Stability at 95° F

Concentration ______ meq/l. Calc. Solubility ______ meq/l. Percent Saturation ______

REMARKS

The sample consisted of one 1 quart glass jar of water.

of these exploratory tests indicated the concentrations used in the final test. All full scale tests included five concentrations and one control sample.

Test fish were transferred from the acclimatizing tanks to the test vessels with small mesh, nylon nets. All transfers were made immediately after preparation of the test dilution. Test fish were not fed for two days prior to the start of full scale tests, nor during the tests. The number of dead fish was recorded exactly at the end of 24, 48 and 96 hour test intervals.

4.7.6 Physical and Chemical Determinations

A complete chemical analysis of a representative sample of the synthetic sea water used for all toxicity determinations is shown in Table 4.7-1 of this report.

4.7.7 Determination of Median Tolerance Limit and Discussion of Results

The median tolerance limit (TL_{50}) is that concentration of the tested material in a suitable experimental water at which 50 percent of the test fish are able to survive for a specified period of exposure. Unless exactly half the fish die in a test, the TL_{50} is determined by a straight line drawn between two test points at two successive concentrations: (1) Where the concentration is lethal to more than half the fish and (2) Where the concentration is lethal to less than half of the test fish.

Figures 4.7-4 through 4.7-11 and Tables 4.7-2 through 4.7-5 show results of the individual toxicity determinations. In each case results of 24 hour, 48 hour, and 96 hour exposures are shown. In accordance with the FWPCA's "interim guide", only the 96 hour determinations are discussed.

A summary of the 96 hour determinations is shown on Table 4.7-6 of this report. Included are the two emulsifiers alone and each of the three test crude samples emulsified with each emulsifier.

Results in general agree with prior published material on toxicity. Most authors[2] agree that 5 to 10 mg/l or more of detergents will cause death. Table 4.7-6 shows a TL_{50} of 9.6 and 14.2 mg/l of I-1751 and I-1752, respectively. Further, Chadwick[3] showed 5 mg/l of Tricon caused no deaths in 48 hours, in line with Table 4.7-2. Although the emulsifiers alone were considerably more toxic than the emulsions, they are present to only 0.5 - 0.8 percent in the emulsions. Taking this dilution factor into account, the toxicity of the emulsifier present in an emulsion is far less than the toxicity of the emulsion. This suggests that the toxicity of the emulsion comes primarily from the oil rather than the emulsifier. To a degree, these conditions might have resulted from the difficulty in keeping the emulsions dispersed in the test liquid. No problem was experienced in keeping the Zueitina crude dispersed in the test sample; however, the higher concentrations of the Tia Juana crude was hard to keep dispersed and difficulty was encountered

TABLE 4.7-2

TOXICITY OF EMULSIFIERS

Initial condition - 10 fish per tank

Concentration (ppm)	Number of Dead Fish 24 hours	48 hours	96 hours
I-1751			
18	9	10	-
15	8	10	-
12	4	8	10
9	2	3	3
6	0	0	0
0 (control)	0	0	0
I-1752			
18	0	4	7
15	0	2	3
12	0	1	3
9	1	2	2
6	0	0	0
0 (control)	0	0	0

FIGURE 4.7-4

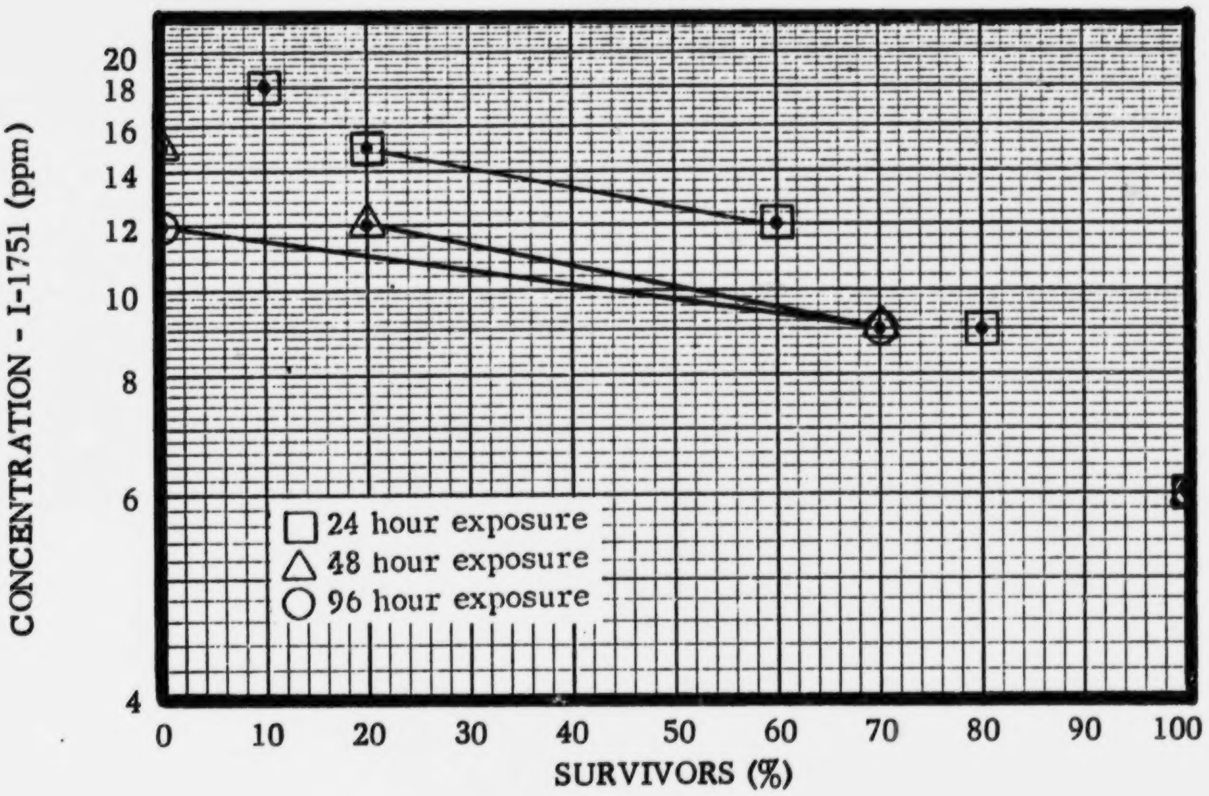


FIGURE 4.7-5

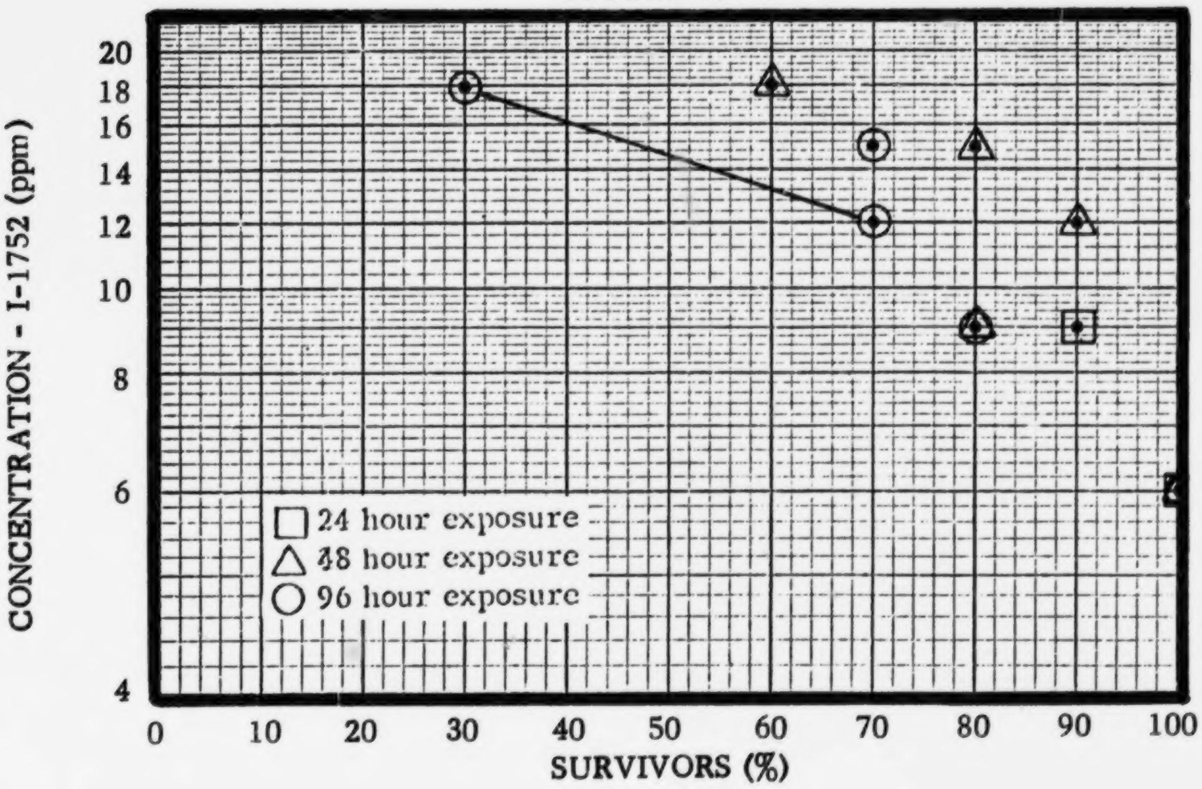


TABLE 4.7-3

TOXICITY OF ZUEITINA EMULSIONS

Emulsion composition:

0.5% Emulsifier

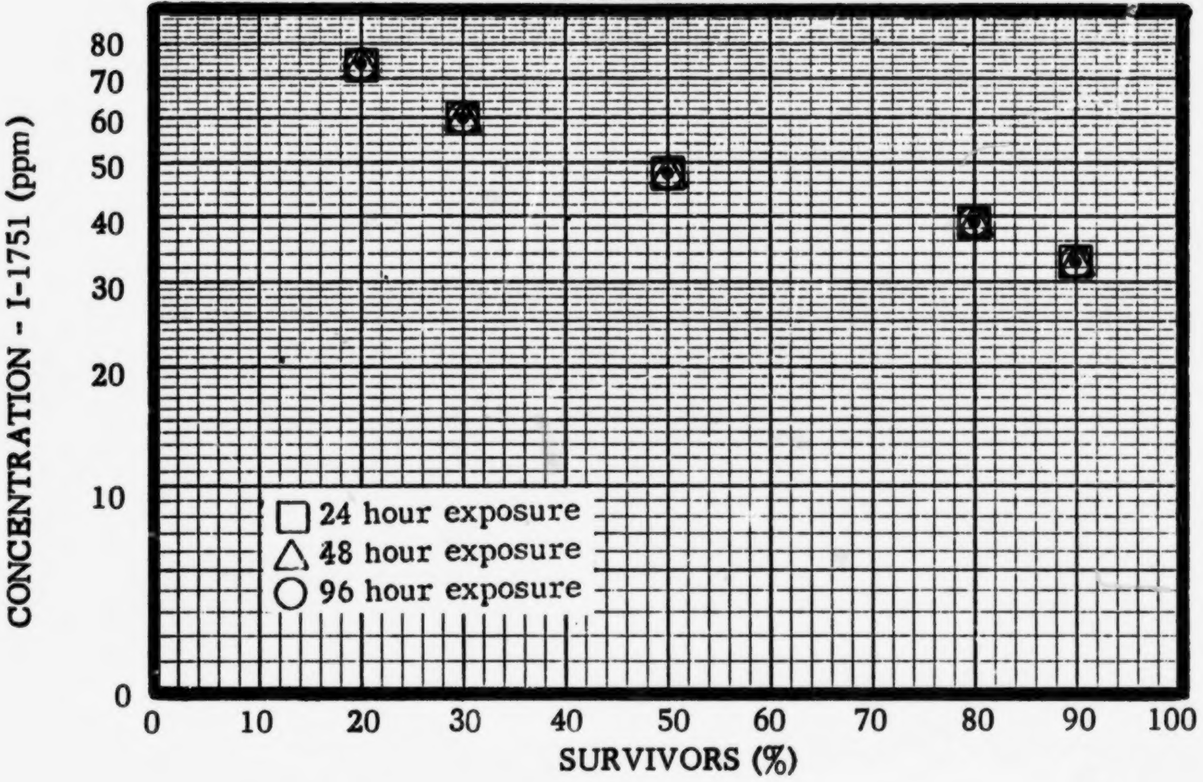
2.5% Water

97.0% Zueitina Crude Oil

Initial condition - 10 fish per tank

Concentration (ppm)	Number of Dead Fish		
	24 hours	48 hours	96 hours
Zueitina emulsified with I-1751			
75	9	9	9
60	8	8	8
48	6	6	6
39	3	3	3
33	2	2	2
0 (control)	1	1	1
Zueitina emulsified with I-1752			
75	9	9	10
60	7	7	7
48	4	4	5
39	2	2	2
33	1	1	1
0 (control)	1	1	1

FIGURE 4.7-6



FIGURES 4.7-7

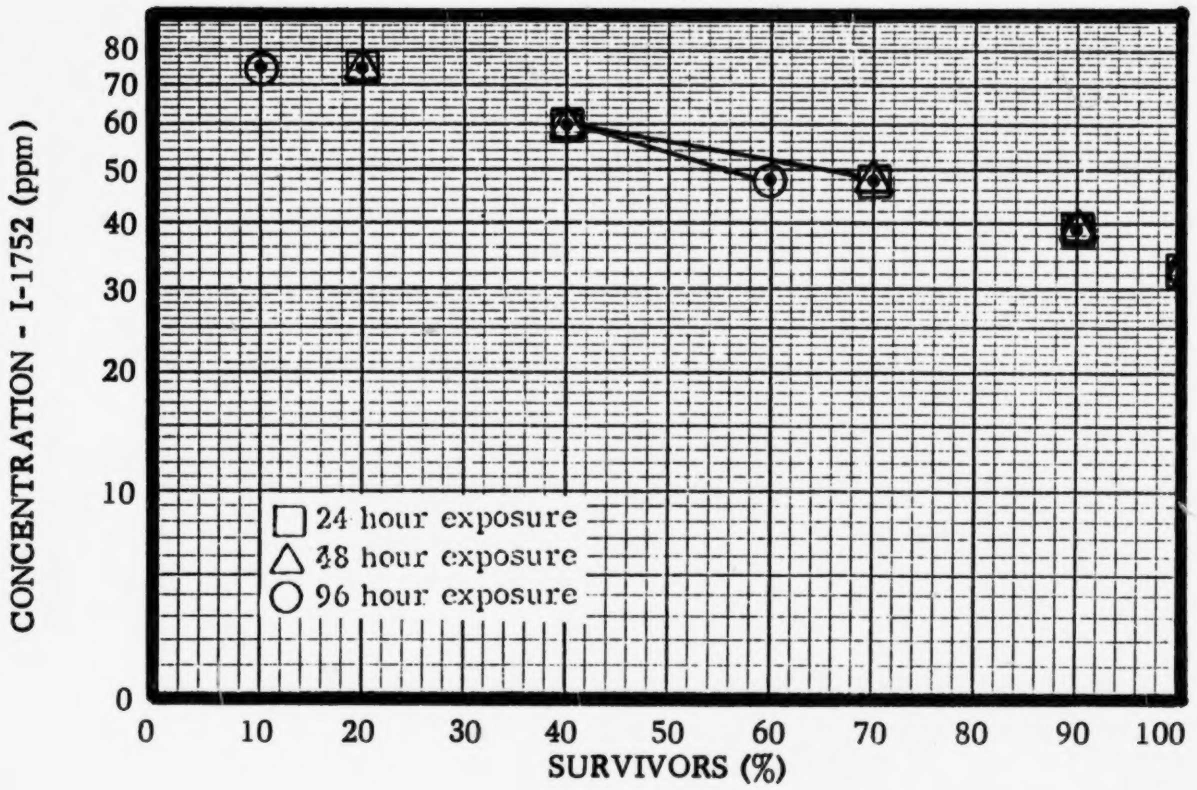


TABLE 4.7-4

TOXICITY OF TIA JUANA EMULSIONS

Emulsion composition:

0.5% Emulsifier

2.5% Water

97.0% Tia Juana Medium Crude Oil

Initial condition - 10 fish per tank

Concentration (ppm)	Number of Dead Fish 24 hours	48 hours	96 hours
Tia Juana emulsified with I-1751			
480	4	5	9
360	4	7	9
240	3	3	4
120	2	2	2
90	0	0	1
0 (control)	0	0	1
Tia Juana emulsified with I-1752			
600	8	8	10
480	3	4	6
360	2	2	4
240	1	1	1
120	0	1	1
0 (control)	0	0	1

FIGURE 4.7-8

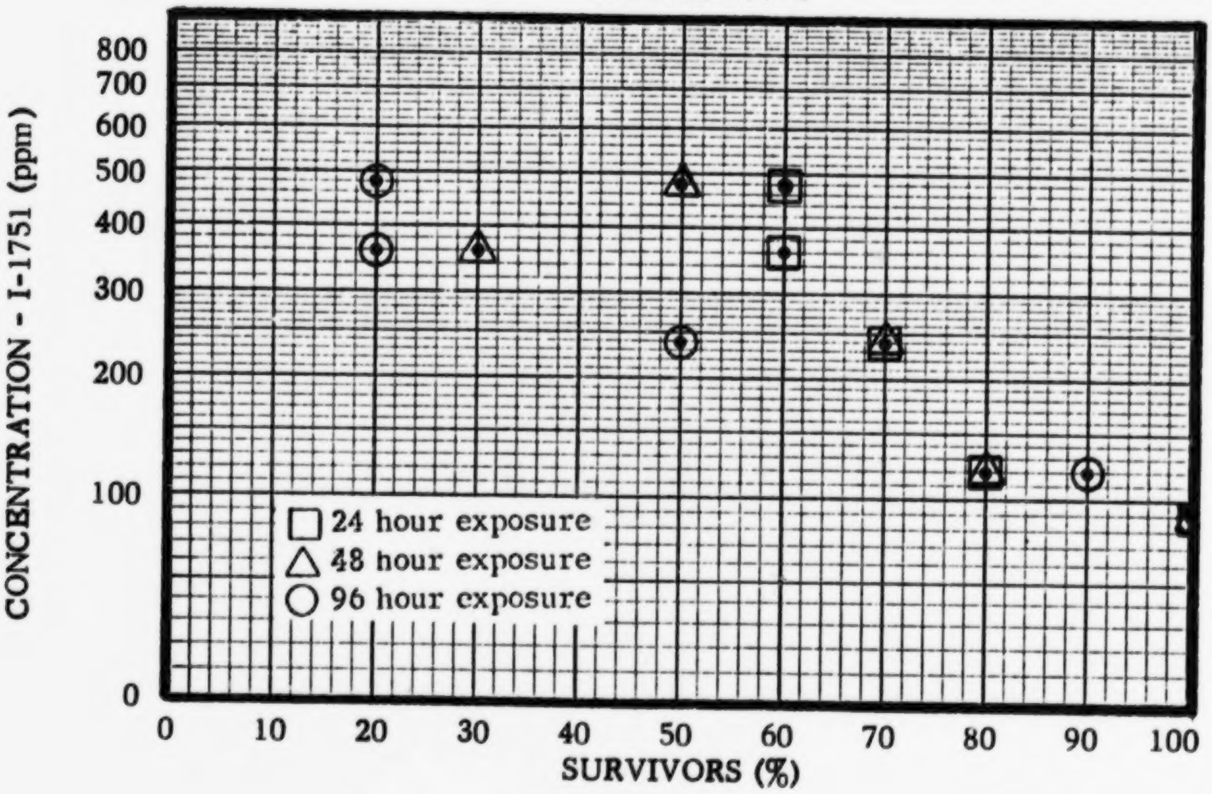


FIGURE 4.7-9

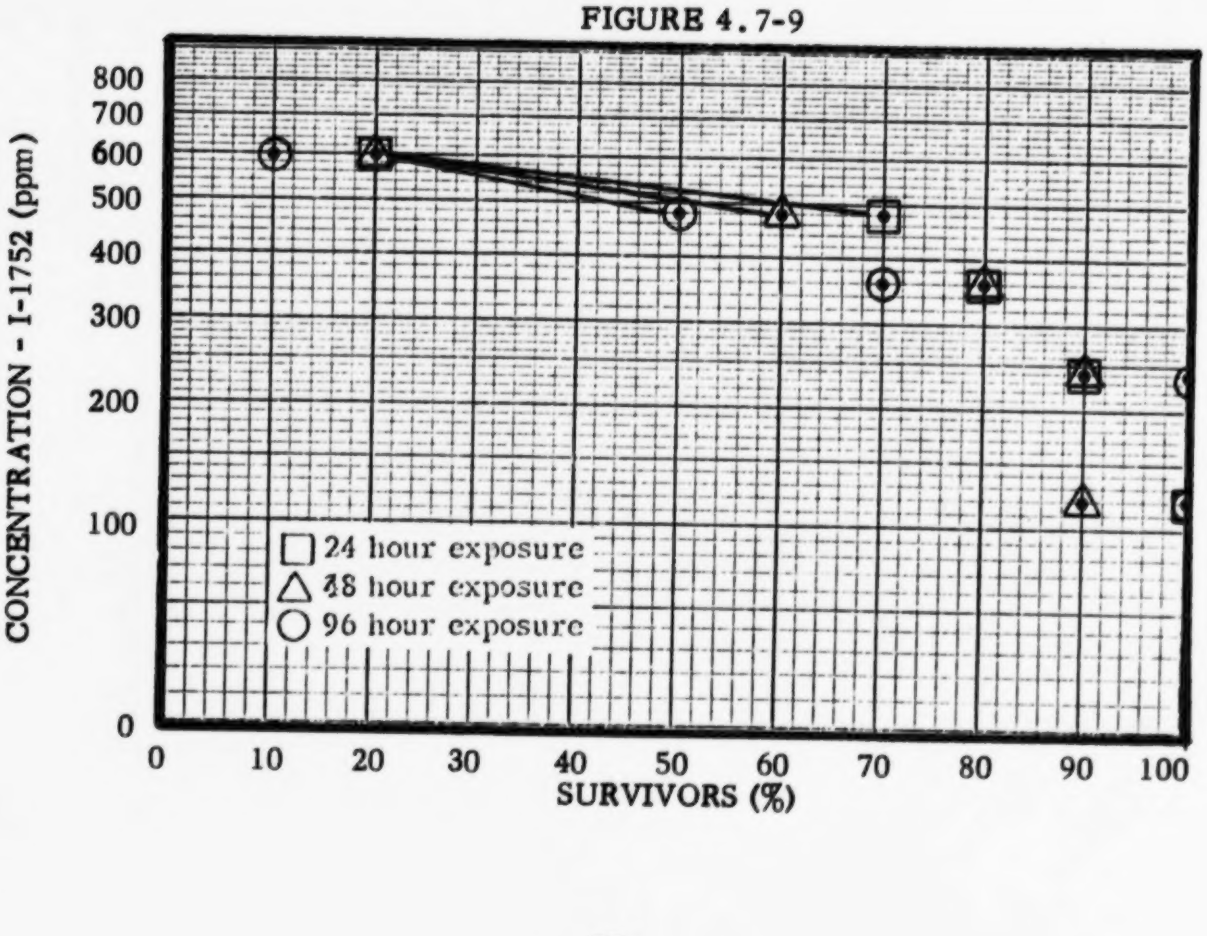


TABLE 4.7-5

TOXICITY OF #6 FUEL OIL EMULSIONS

Emulsion composition:

0.8% Emulsifier

2.2% Water

97.0% #6 Fuel Oil

Initial condition - 10 fish per tank

Concentration (ppm)	Number of Dead Fish 24 hours	48 hours	96 hours
#6 Fuel Oil emulsified with I-1751			
900	7	9	10
800	4	5	5
700	3	4	4
600	2	2	2
500	0	1	1
0 (control)	0	0	0
#6 Fuel Oil emulsified with I-1752			
900	6	7	9
800	4	4	5
700	3	3	4
600	1	2	2
500	0	0	0
0 (control)	0	0	0

TOXICITY OF #6 FUEL OIL EMULSIONS

FIGURE 4.7-10

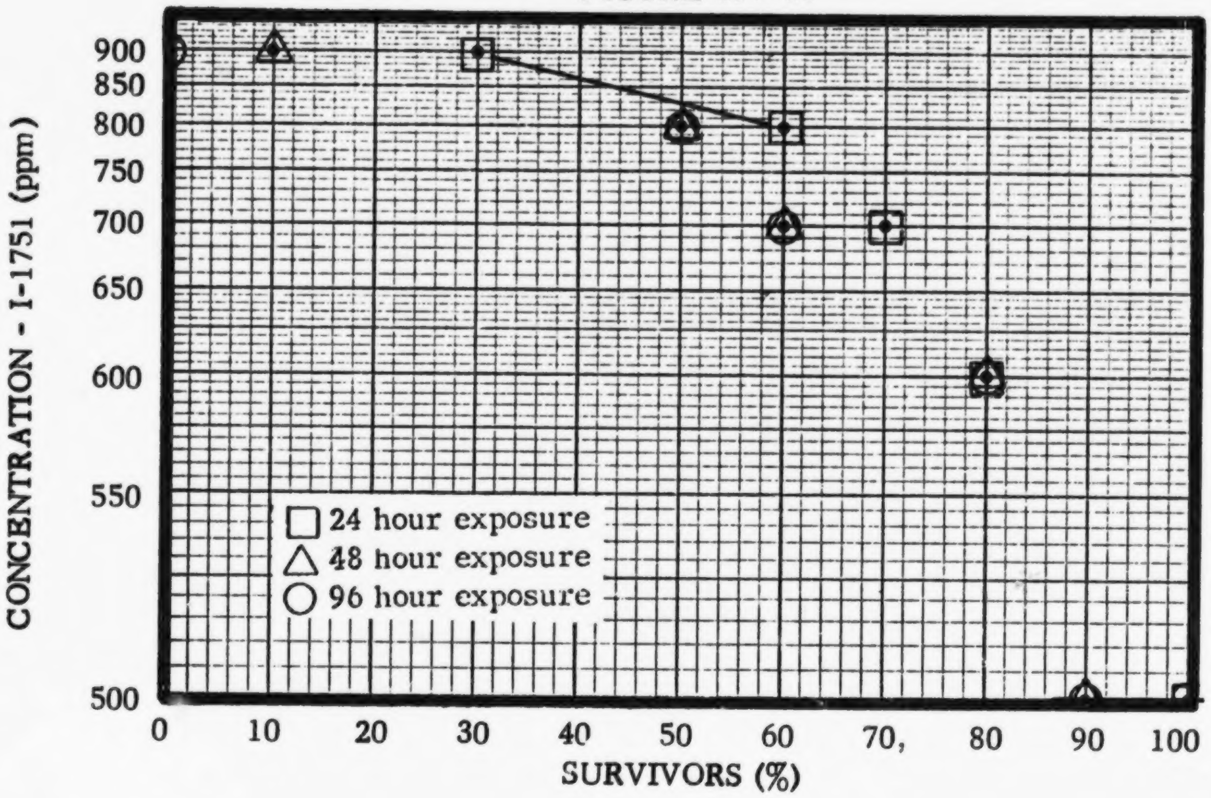


FIGURE 4.7-11

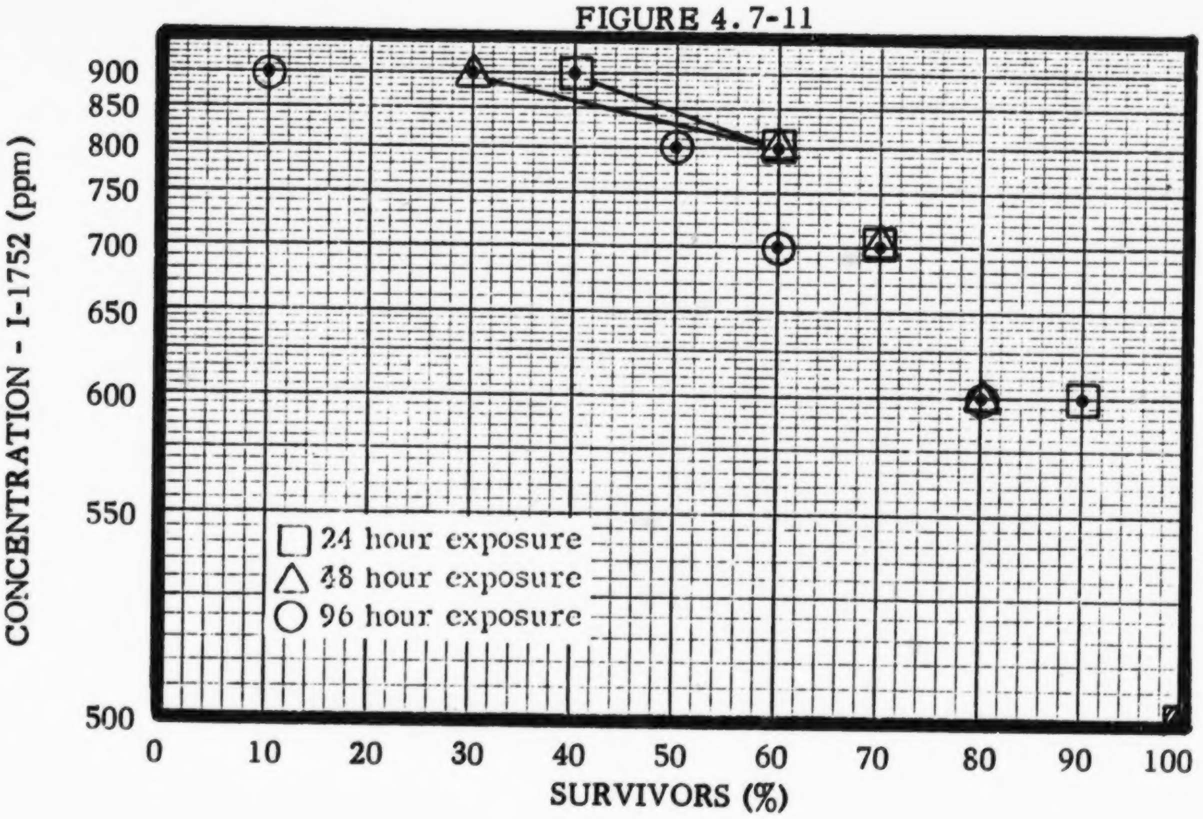


TABLE 4.7-6

SUMMARY OF NINETY-SIX HOUR TL_{50} VALUES

Emulsifier or Emulsion	TL_{50} Concentration (mg/l)
I-1751 (Emulsifier)	9.6
I-1752 (Emulsifier)	14.2
Zueitina crude with I-1751	48.0
Zueitina crude with I-1752	54.0
Tia Juana crude with I-1751	240
Tia Juana crude with I-1752	480
#6 Fuel Oil with I-1751	800
#6 Fuel Oil with I-1752	800

with all concentrations of #6 Fuel Oil. Some free oil was present on the surface of the test liquid with the three higher Tia Juana concentrations and all of the #6 Fuel Oil concentrations after 80 hours of testing.

The Zueitina, high API gravity crude, emulsion was substantially more toxic than the other lower API gravity crude emulsions. These results are in agreement with results reported by other investigators that lighter hydrocarbon ends are more soluble in water and contribute to a higher level of toxicity. Thus, Tagatz found heavier oils substantially less toxic than light oils.

Emulsification may increase the toxicity of oil, when higher concentrations are present. The level of toxicity found for #6 Fuel Oil, for example, was substantially less than was found for emulsifier #6 Fuel Oil(2,000 mg/l[7] vs 800 ppm[8]). It may be that oil alone, which tends to stay on the water surface, is less toxic to fish than oil emulsion dispersed through the water, where it may come into more intimate contact with the fish.

The mechanism of fish poisoning by oil is not clear. It may be purely a mechanical effect of oil coating the gills. There is some indication that the presence of detergents increases the absorption of oil constituents by fish. Also, there is some evidence that the presence of salt reduces the toxicity of detergents.

In summary, the toxicity of the emulsions varies with the oils emulsified. The lighter, higher API gravity, oils are more toxic than the heavy oils. The emulsifiers apparently dispersed the oils completely and brought the oils into intimate contact with the fish, thus lowering the TL_{50} level below that which might be expected for oils along. However, in actual sea conditions, the emulsion would be rapidly dispersed to below the toxic level.

4.8 Consideration of Break-Back Methods

4.8.1 Introduction

Although quantitative studies of the equipment and cost necessary to break-back the emulsion when received at the refinery are not a part of this study, some preliminary tests were made, and certain qualitative comments can be made.

4.8.2 Pumps

Some studies[1] indicate that emulsified fuel can be broken back by a high speed centrifugal pump, or by recirculation through a gear pump. Complete break-back was obtained at 4,200 rpm, even with 1.5 percent emulsifier present. Prior studies on atomization have indicated that an emulsion containing 1.5 percent emulsifier was much more stable than one containing 1.0 percent emulsifier. Since the present study uses 0.5 to 0.8 percent emulsifier, this would suggest that these emulsions may break-back under these conditions. Since pumps are needed to unload the ship in any case, the only extra cost would be added pump and power costs due to the high speed. Extrapolation from 3,600 rpm pump charts indicates that 1,600 hp would be required for 400 psi at 100 barrel per minute. This would add approximately 0.2 cents per barrel to the cost. Separation of external phase from the crude oil in the broken emulsion should occur in the storage tanks, or might be expedited by use of centrifuges.

4.8.3 Atomization

Bench type tests, flowing through an ultrasonic atomizer indicated that a Tia Juana emulsion could be broken back to about 80 percent oil, 20 percent emulsion (see Table 4.8.1). However, nearly a day's standing was required to achieve the separation. Published work[1] indicates that atomization of emulsion at 400 psi with one percent emulsifier persent can give complete emulsion break-back. With 1.5 percent emulsifier only 95 percent break-back was obtained. Thus with the 0.5 percent emulsifier as used in our studies complete break-back would be expected if results are similar to those found in this published data. The cost of this operation would be comparable to that for the high speed pumps discussed in 4.7.2, less than one cent per barrel.

4.8.4 Ultrasonic Break-Back

Ultrasonic treatment of an emulsion tends to break it back approximately to the "seed" condition - free oil plus an emulsion containing 70 percent oil and 30 percent external (aqueous) phase. A 30 minute ultrasonic batch treatment followed by one day standing gave 86 percent clear oil and 14 percent emulsion. Treatment with a 150 watt, 28 kilohertz homogenizer, at a rate of 45 milliliters per minute, followed by 15 minutes settling gave 86 percent oil and 14 percent emulsion.

4.8.5 Chemical Break-Back

It is well known that strong, particularly polyionic, electrolytes rapidly agglomerate emulsions. Successful use of this method on fuel emulsions has been reported[1].

Tests were made with 0.6 percent II-0521 Electro-Chem demulsifier, and 2.4 percent water mixed with emulsion and allowed to stand one day. Break-back was complete. The cost of this chemical approach would be much greater than that of a mechanical approach, if the latter is effective.

4.8.6 Re-Use of "Emulsion Seed" or Water Phase

In cases in which tankers do not have a cargo for the return trip, it may well be economically attractive to carry the external phase (3 percent of the emulsion) back to a loading dock to be used again, thereby reducing the chemical cost, which is the most costly single item in the emulsification operation. An alternative would be to carry back the "emulsion seed", which would be desirable if difficulties arise in completely breaking the emulsion. However, the 7.5 percent of the oil cargo present in the returned "emulsion seed" might represent a prohibitive loss in tanker capacity. The continuous phase of the emulsion alone represents only a 3 percent loss in cargo capacity, and this would be offset by reduced ship leakage, reduced volatility and reduced hazards.

4.8.7 Discussion

Based on published data, the mechanical action of pumps, with return of external phase for reuse, holds the greatest promise of emulsion break-back. However, because of differences between oils and emulsifiers any confidence in these procedures would require tests with the materials of interest.

TABLE 4.8.1

EMULSION SEPARATION FOLLOWING ATOMIZATION

Separation of oil from emulsion when Tia Juana was flowed through an ultrasonic atomizer, collected in a graduate and allowed to settle.

Settling Time (hours)	%Oil	% Emulsion
0.16	30	70
0.50	60	40
1.00	68	32
24.00	79	21

4.9 Product Alteration

4.9.1 Method

The maintenance of product intergrity is vital to the economics of this concept for handling and transporting oil. Standard ASTM tests, used to determine the basic characteristics of refinery feed stock, have been made on the three test oils.

Test performed were:

1. Distillation (ASTM D 285)
2. Gravity
3. Viscosity

These tests were performed on each oil "as received" and repeated on the "reclaimed oil". The test data shown for "reclaimed oil" represent the conditions after ultrasonic emulsification and then subsequent chemical demulsification.

The distillation tests, which in effect show the hydrocarbon make up of the oil, were included to evaluate any changes in the marketable hydrocarbons. The API gravity, viscosity, vapor pressure, and flash point tests provide additional definition of basic characteristics.

Water soluble solids and ash content were determined to evaluate the alteration or removal of substances without process value. Any removal of these materials represents upgrading of the oil.

4.9.2 Product Alteration Data

Results of product alteration tests are shown on Table 4.9-1 and Figure 4.9-1.

4.9.3 Discussion of Product Alteration

The distillation tests show no change in the basic character of the three oils. All "as received" and "reclaimed" temperatures are the same except for five or six, which are considered within test accuracy. No light or volatile fractions have been lost as a result of the emulsification/demulsification process.

The API gravity and the viscosity remained the same. These data support the distillation results. Also, they indicate that no extraneous materials were detected after reclaiming.

One significant change in each of the three oils did result from the emulsification demulsification process. The concentration of water soluble solids, including salt, was reduced. This material was reduced in the Zueitina crude from 80 mg/l to 20 mg/l or about 75 percent; in the Tia Juana crude by about 83 percent and in the #6 Fuel Oil by 94 percent.

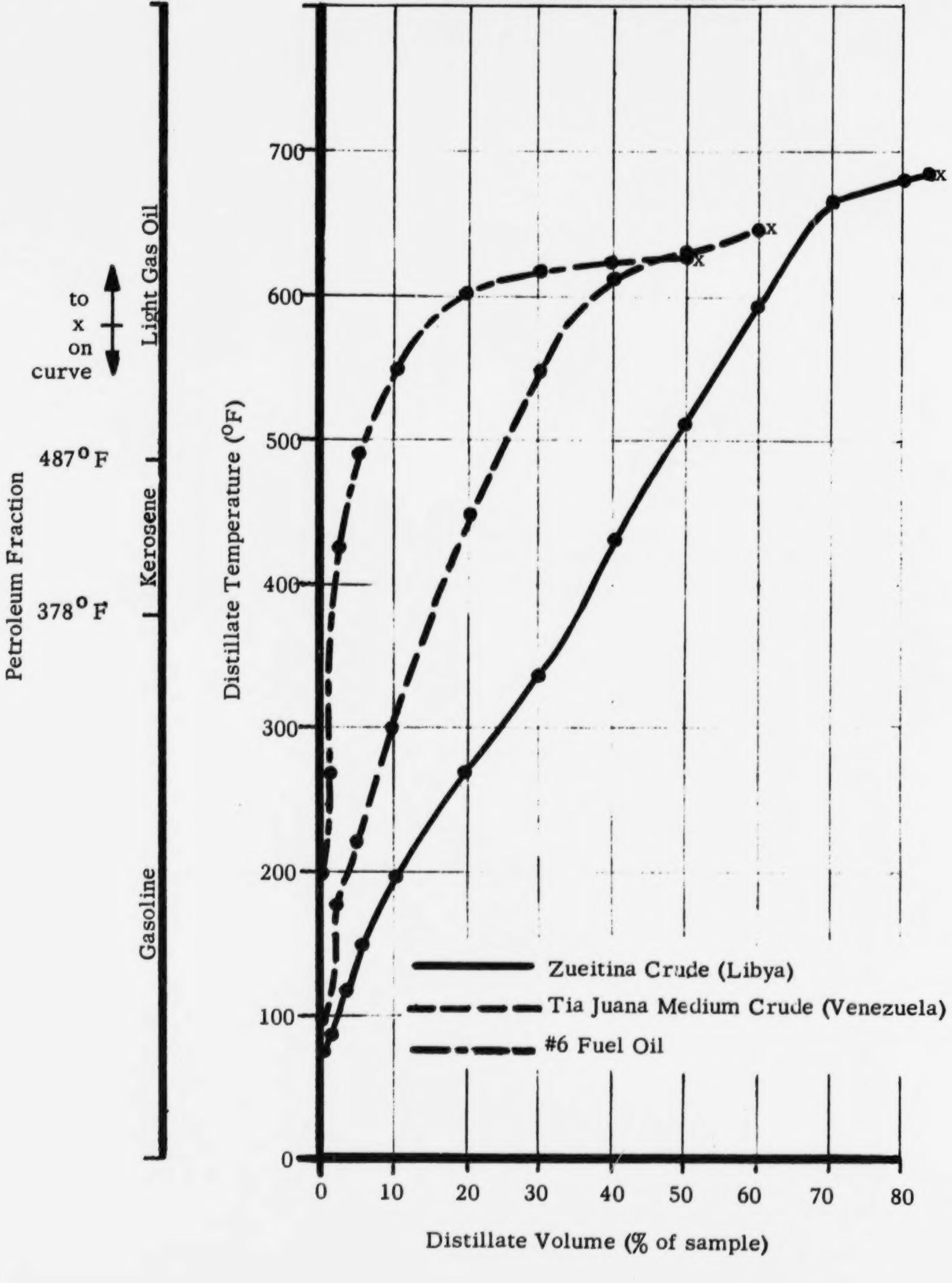
The above data also suggest the emulsion particles are very small. Considering the small volume of water used in the emulsion and the brief contact time during these tests, there must be intimate mixing to achieve any real solution of salts.

In summary, the oils were not altered in any manner that could be considered detrimental. There was some upgrading of the oils by removal of various salts.

TABLE 4.9-1

Characteristic	Zueitina Crude (Libya)		Tia Juana Medium Crude		No. 6 Fuel Oil	
	As Received	Reclaimed	As Received	Reclaimed	As Received	Reclaimed
Distillation						
Initial Boil Point (I. B. P. °F)	76	79	86	85	194	192
1% (°F)	80	82	110	109	266	265
3% (°F)	120	121	178	178	425	424
5% (°F)	144	145	220	220	487	486
10% (°F)	196	196	296	296	550	550
20% (°F)	267	267	445	445	602	602
30% (°F)	336	336	548	548	612	612
40% (°F)	428	428	610	610	614	613
50% (°F)	508	508	628	628	614	614
60% (°F)	590	590	642	642	-	-
70% (°F)	660	660	-	-	-	-
80% (°F)	680	680	-	-	-	-
End Point (°F)	682	684	642	642	614	614
Gasoline, I. B. P. - 378°F (%)	33.3	33.3	15.3	15.3	2.0	2.0
Kerosene, 378 - 487°F (%)	13.8	13.8	8.8	8.8	3.0	3.0
Light Gas Oil, 487°F - End Point (%)	40.2	40.2	46.7	46.7	51.7	51.7
Residue (%)	10.7	10.7	29.2	29.2	43.3	43.3
Gravity (°API at 60°)	41.8	41.7	24.3	24.3	8.3	8.3
Viscosity (cp at 75°F)	3.4	-	26.0	-	3490	-
Viscosity (cs at 75°F)	4.2	4.2	28.8	28.7	3470	3450
Viscosity (Saybolt Univ. at 100°F)	-	-	160	-	-	-
Viscosity (Saybolt Furol at 122°F)	-	-	-	-	126	-
Reid Vapor Pressure (lbs. at 100°F)	8.2	7.6	4.2	4.1	0.4	0.4
Pour Point (°F)	30	30	-50	-50	35	35
Flash Point (P. M., °F)	42	44	64	64	220	220
Paraffin (% wt.)	26	26	15	15	13	13
pH of Water Extract	-	-	-	-	2.0	6.1
Water Soluble Solids (mg/l)	80	20	100	17	20	1.2
Sodium Chloride (mg/l)	4.5	1.2	19.1	1.8	12	0
Water (%)	0.0	0.1	0.2	0.1	1.0	0.6
Sulfur (%)	0.2	0.1	1.8	1.6	-	-
Hydrogen Sulfide or Mercaptan Oder	Present	Absent	Present	Absent	-	-
Ash (%)	0.006	0.004	2.75	1.84	7.41	4.62

FIGURE 4.9-1
OIL DISTILLATION CURVES



5. DESIGN, CONSTRUCTION & OPERATION OF BENCH SCALE EMULSIFICATION UNIT

5.1 Basis of Design - Prior Work

The design of the bench scale emulsification unit was based on prior work done with a small system capable of producing about one quart per minute of finished emulsion, knowledge of emulsification system design and the proprietary emulsification method of the contractor.[1]

5.2 Design and Construction of Bench Scale Unit

Figure 5-1 is a schematic drawing and Figure 5-2 is a photograph of the laboratory pilot model bench scale emulsification system used to determine the feasibility of and design requirements for an emulsification system large enough to be employed at modern tanker loading facilities. This unit had a maximum emulsification capacity of six gallons per minute.

An air compressor was used to supply power for the mechanical blending devices. A positive displacement pump was used to supply oil at a constant rate from oil storage (55 gallon drums) to the manifold. The manifold was equipped with twelve stations, each having an on/off valve and a flow rate control valve. Station twelve was connected to the "emulsion seed" premix unit. Seven percent (by volume of finished emulsion) of oil was metered into the premix chamber where it was emulsified with a three percent mixture of water and emulsifier.

The premix unit (Figure 5-3A) was a cylinder four inches deep with a three inch inside diameter. Two one and three-fourths inch propellers of opposing 30 degree pitch were mounted one inch apart in the middle of a one-fourth inch shaft and was powered by a small air motor, through a gear train which provided a propeller speed of approximately 1,800 rpm.

The premixed "emulsion seed" was transferred to the ultrasonic homogenizer with a positive displacement pump. The ultrasonic homogenizer, (Figure 5-3B) developed and used in this study, was based on a new concept, and differed considerably from the homogenizer normally used by the contractor. For this system a 28 kilohertz, 150 watt, flat plate, immersible transducer was modified by placing a cover plate one-sixteenth of an inch from the transducer plate surface (see Appendix II for disclosure of invention). The cover plate was tapped at each end to allow emulsion flow. As the "emulsion seed" flowed across the vibrating plate, the dispersed oil was broken into uniform droplets of approximately one micron diameter. Seven volumes of these droplets were dispersed in three volumes of water and emulsifier to make up the "emulsion seed". The ultrasonic

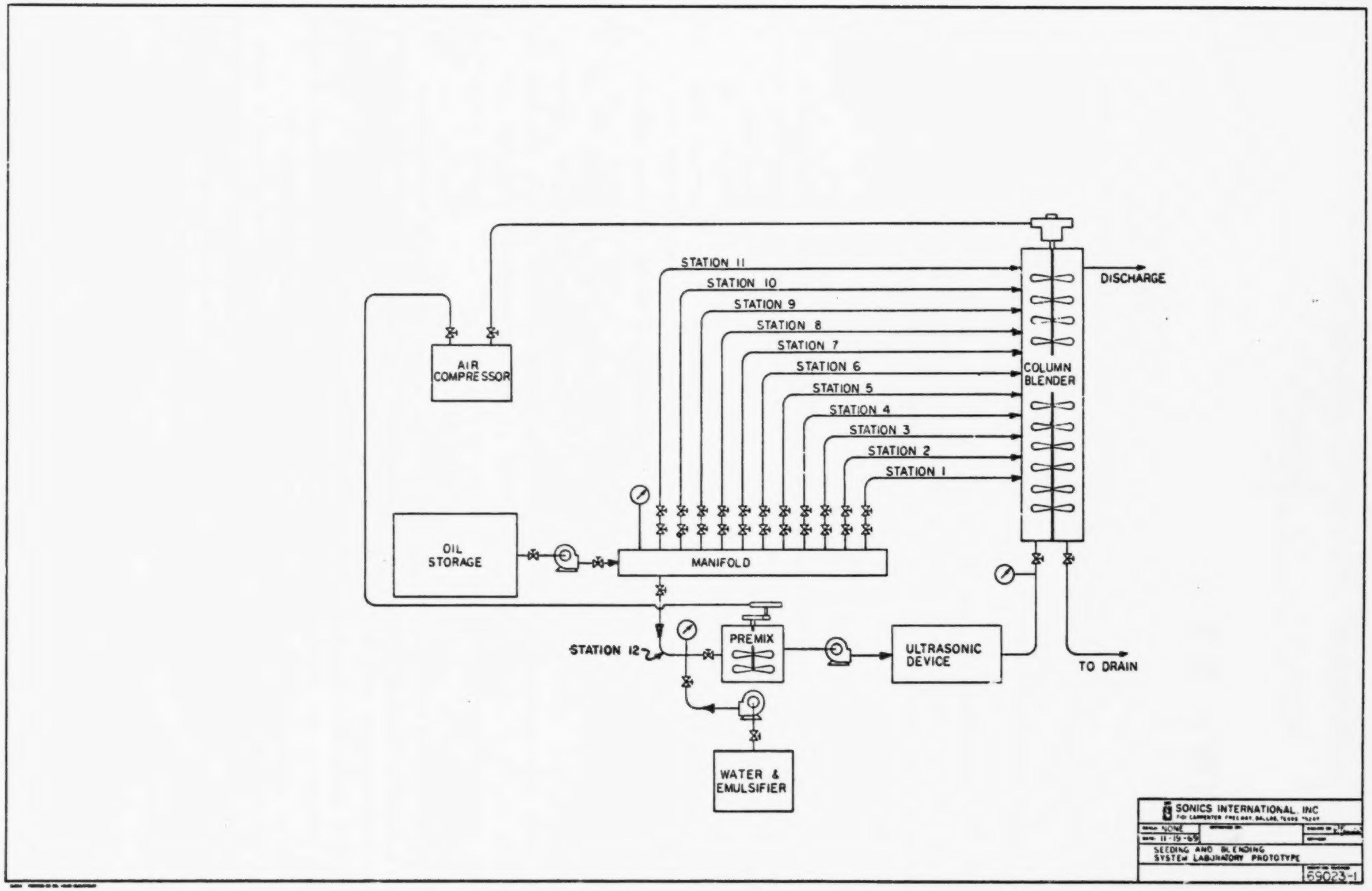

AIR COMPRESSOR
OIL STORAGE
MANIFOLD
STATION 11
STATION 10
STATION 9
STATION 8
STATION 7
STATION 6
STATION 5
STATION 4
STATION 3
STATION 2
STATION 1
COLUMN BLENDER
DISCHARGE
TO DRAIN
STATION 12
PREMIX
ULTRASONIC DEVICE
WATER & EMULSIFIER
SONICS INTERNATIONAL, INC
NONE
11-19-69
SEEDING AND BLENDING SYSTEM LABORATORY PROTOTYPE
69023-1

FIGURE 5-1 BENCH SCALE EMULSIFICATION SYSTEM SCHEMATIC

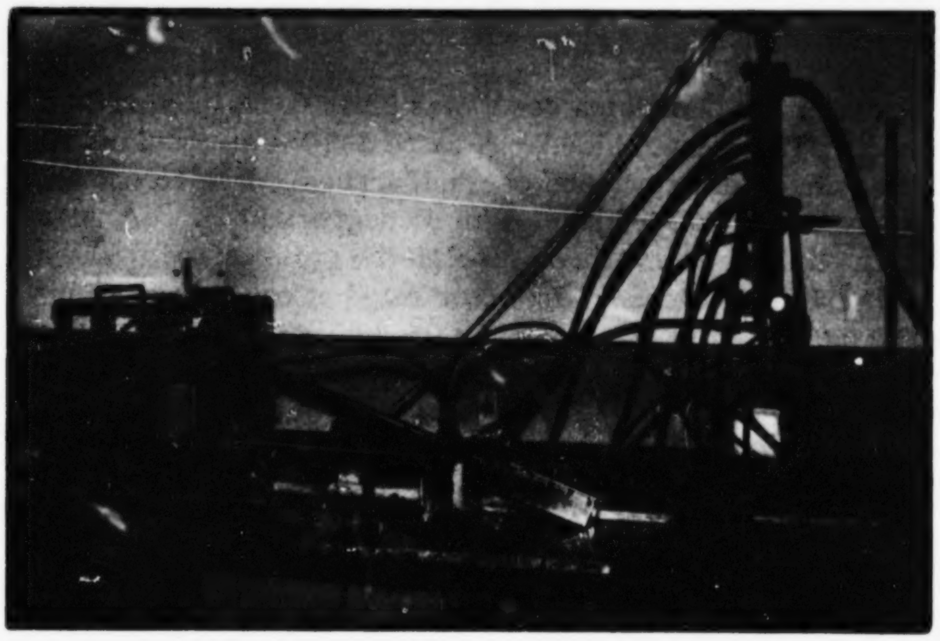


Figure 5-2 Bench Scale Emulsification System

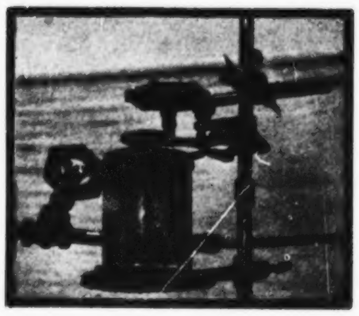


Figure 5-3A
"Emulsion Seed" Premix Unit
of Bench Scale System

homogenizer was powered by a converter designed for a 60 cycle, 110 volt alternating current input.

From the homogenizer the "emulsion seed" was piped to an inlet at the base of the column blender. The column blender (Figure 5-3C) was a cylinder 24 inches high with an inside diameter of two and one-half inches. Twelve one and three-quarters inch diameter propeller blades with 45 degrees pitch were mounted on a one-quarter inch shaft which extended through the cylinder top to the air motor power source. The column blender air motor rated at one-half horsepower at 2,000 rpm and 90 psi pressure was driven at speeds of from 2,700 to 3,700 rpm during the tests. The propeller blades were mounted to provide a pumping action toward the top of the column. The bulk of the oil (90 percent) was introduced into the column blender through Manifold Stations 1 through 11, which entered the column at regular intervals from near the base to near the top of the column. The flow through Station 1 was about 1 percent of the column effluent, and flow was progressively increased at each successive station, except Station 11, where it was decreased from the flow-through Station 10. In the column the oil was blended into the "emulsion seed" to produce the finished 97 percent oil-in-water emulsion.

A bypass was added to each of the supply pumps to permit operation of the unit at various output rates. Calculations were made for output rates from two to five gallons per minute. Table 5-1 gives the calculated flow rates for the seed and Table 5-2 gives the calculated flow rates for the oil.

Construction materials were selected on the basis of cost, machinability and versatility. Clear acrylic was used for the column and the homogenizer cover plate to provide the advantage of visual observations of the effectiveness of each piece of equipment. Plastic tubing and nylon fittings were used where possible.

5.3. Operation of Bench Scale Unit and Data Collection

The emulsification system was operated on a continuous flow basis and was capable of shutdown and subsequent starting without system cleanup or flushing. It was possible to switch from one oil emulsion to another with only a few gallons of waste emulsion resulting. Once the oil flow rates into the column blender and the corresponding seed ratios were adjusted, the emulsification unit worked efficiently. Careful adjustment of the flow rates was essential to prevent carry-over of free oil. If an excess of oil was introduced during the early blending stages (through the lower inlets to the column), the column was "flooded" and normal blending action was inhibited. To maintain proper blender action the oil had to be fed to each inlet at a rate that would permit nearly complete blending into the emulsion before the emulsion rose to the next inlet of the column. As shown in Table 5-2, the inlet flow rate was progressively increased from the lower to the higher inlets, successively, except for the decrease at Station 11.

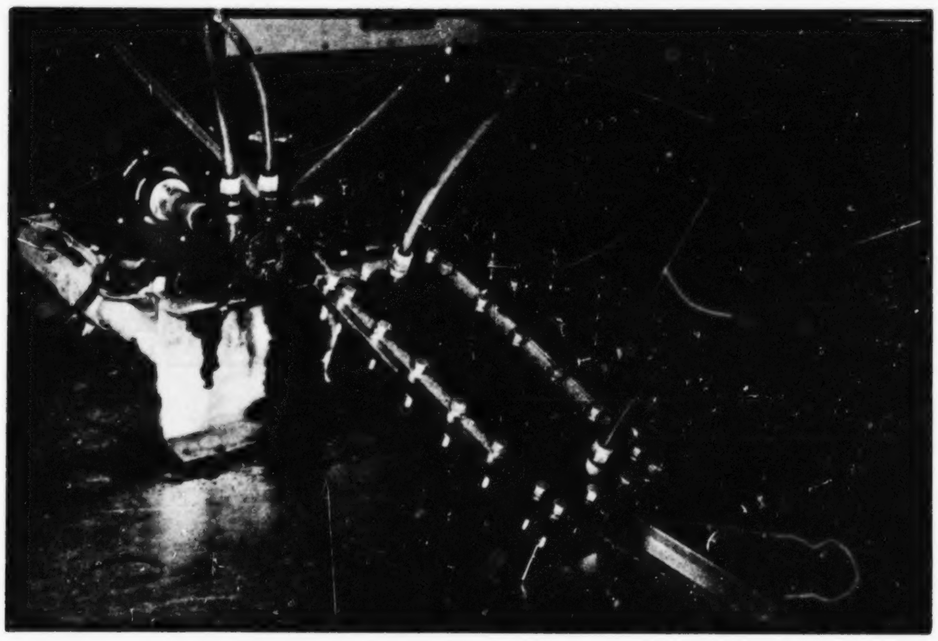


Figure 5-3B Flat-Plate Homogenizer, Bench Scale System

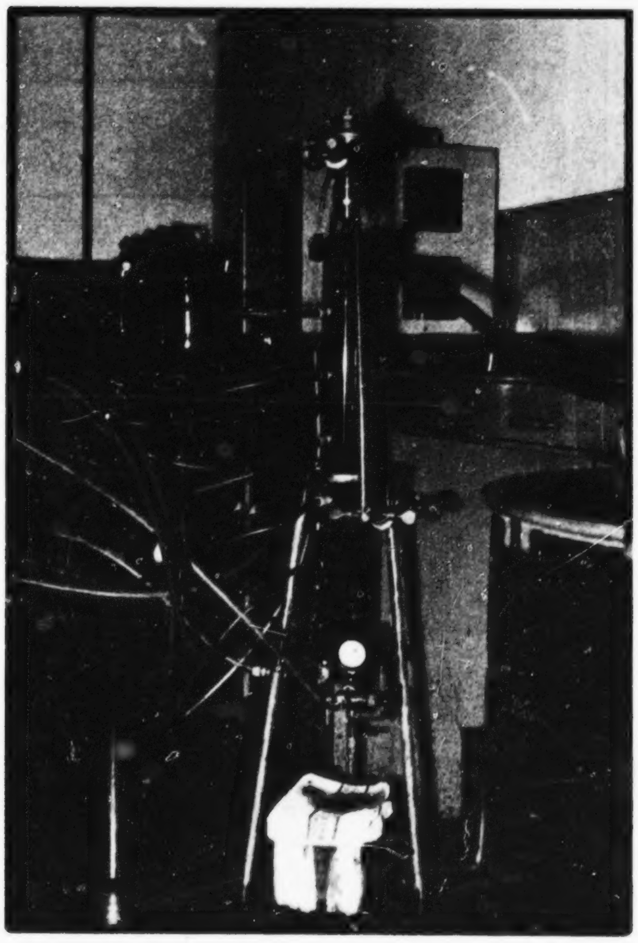


Figure 5-3C
Column Blender
of Bench Scale System

TABLE 5-1

BENCH SCALE EMULSIFICATION UNIT

"EMULSION SEED" RATES FOR 2 TO 5 GALLONS PER MINUTE

	2 gpm			3 gpm			4 gpm			5 gpm		
	gal	in^3	l	gal	in^3	l	gal	in^3	l	gal	in^3	l
EMULSIFIER	0.010	2.31	0.038	0.015	3.47	0.055	0.020	4.62	0.076	0.025	5.77	0.095
WATER	0.050	11.55	0.189	0.075	17.33	0.284	0.100	23.10	0.379	0.125	28.88	0.470
OIL	0.140	46.20	0.531	0.210	48.51	0.793	0.280	64.68	1.060	0.350	80.85	1.320
TOTAL	0.20	46.2	0.758	0.30	69.3	1.140	0.40	92.40	1.515	0.050	115.50	1.900

TABLE 5-2

BENCH SCALE EMULSIFICATION UNIT

BLENDER INLET OIL RATES FOR 2 TO 5 GALLONS PER MINUTE

IN NO.	%	2 gpm			3 gpm			4 gpm			5 gpm		
		gal	in^3	l	gal	in^3	l	gal	in^3	l	gal	in^3	l
1	1	.018	4.2	.068	.027	6.24	.102	.036	8.4	.136	.045	10.5	.170
2	2	.036	8.4	.136	.054	12.60	.204	.072	16.8	.273	.090	21.0	.341
3	3	.054	12.6	.204	.081	18.70	.307	.108	24.9	.409	.135	31.3	.511
4	5	.090	15.3	.341	.135	31.19	.511	.180	41.5	.681	.225	46.4	.852
5	7	.124	29.4	.469	.189	44.26	.715	.248	57.3	.939	.315	73.7	1.192
6	10	.180	42.0	.681	.270	62.37	1.022	.360	83.2	1.363	.450	104.4	1.703
7	11	.198	46.2	.741	.297	68.60	1.086	.396	91.4	1.496	.495	114.8	1.874
8	12	.216	50.4	.818	.324	74.84	1.226	.432	99.8	1.635	.540	125.2	2.044
9	12	.216	50.4	.818	.324	74.84	1.226	.432	99.8	1.635	.540	125.2	2.044
10	13	.234	54.6	.886	.351	81.08	1.329	.468	108.1	1.771	.585	135.7	2.214
11	14	.254	58.8	.961	.378	87.32	1.430	.508	117.4	1.922	.630	146.0	2.385
12	10	.180	42.0	.681	.270	62.37	1.022	.360	83.2	1.363	.450	104.4	1.703
TOTAL:		1.800	414.3	6.809	2.700	624.40	10.180	3.600	831.8	13.620	4.500	1039.5	17.030

The finished emulsion outlet of the column was immediately preceded by the last oil inlet. Therefore, it was necessary to maintain the oil flow into the top inlet at a point lower than that of the other upper inlets, to prevent carry-over of unblended free oil.

Six recorded runs were made. One run was made with Zueitina crude oil, three runs with Tia Juana Medium crude oil, one run with #6 Fuel Oil and one run with #2 Diesel Fuel. The following data were collected during each recorded run:

1. Blender Motor Air Pressure
2. Oil Inlet Pressure
3. Seed Inlet Pressure
4. Blender Motor Speed
5. Ambient Temperature
6. Emulsion Discharge Temperature
7. Blender Outlet Flow Rate

Figures 5-4 through 5-26 and Tables 5-3 through 5-8 give graphic and tabular presentations of the data collected during these six runs.

5.4 Discussion of Bench Scale Emulsification

The bench scale emulsification unit was designed and operated to provide the information needed for the conceptual design of the basic 100 barrel per minute unit. The unit was designed for maximum flow control flexibility to accommodate a broad range of oil characterisitics and to provide as much basic data as possible.

The power requirements were determined by monitoring the air motor speed and the line pressure at the air motor. The air motor was rated one-half horse-power at 2,000 rpm with 90 psi line pressure. The motor had sufficient power for blending all the emulsions made during this study.

System pressures and temperatures were monitored to provide data for material requirements for scale-up.

The system flow rate was monitored to indicate system capabilities and provide a basis for calculations of the projected economics of constructing and operating a scale-up.

Demonstration runs were made with #2 Diesel Fuel because it was readily obtained, relatively inexpensive and emulsified readily by the bench scale system due to its "average" characteristics.

The data presented by Tables 5-3 through 5-8 and Figures 5-4 through 5-26 indicate

TABLE 5-3

EMULSIFICATION PILOT MODEL DATA

TEST RUN - ZUEITINA CRUDE

READING NO.	AIR PRESS MOTOR PSI	AIR MOTOR RPM	MANIFOLD INLET PRESS PSI	SEED OUTPUT PRESS PSI	EMULSION FLOW RATE LIT/MINUTE	ROOM TEMP. (°F)	EMULSION DISCHARGE TEMP. (°F)
1	70	3700	35	5	18.0	71.0	79
2	63	3406	35	7	17.5	71.0	79
3	61	3235	35	7	16.0	71.0	79
4	58	3270	35	9	16.0	71.0	79
5	56	3420	35	13	16.0	71.0	79
6	53	3365	35	13	16.0	71.0	79
7	51	3395	35	13	16.0	71.0	79
8	50	3297	35	13	16.0	71.0	79
9	48	3231	35	13	16.0	71.0	79
10	48	3231	35	13	16.0	71.0	79

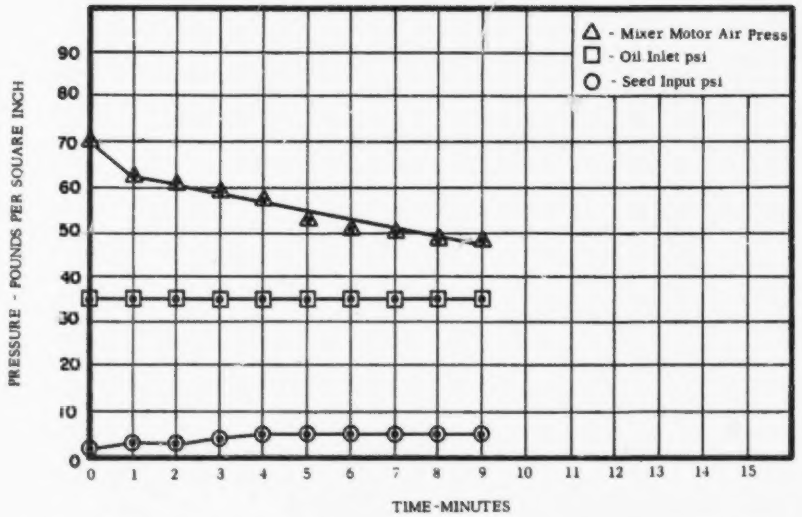


FIGURE 5-4 MIXER AIR MOTOR PRESSURE, OIL & SEED OUTPUT PRESSURE ZUEITINA CRUDE

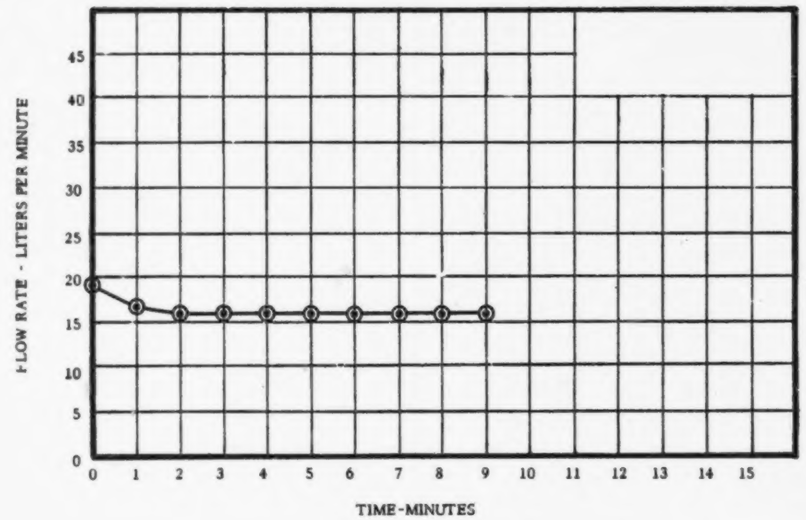


FIGURE 5-5 MEASURED FLOW RATE, ZUEITINA CRUDE

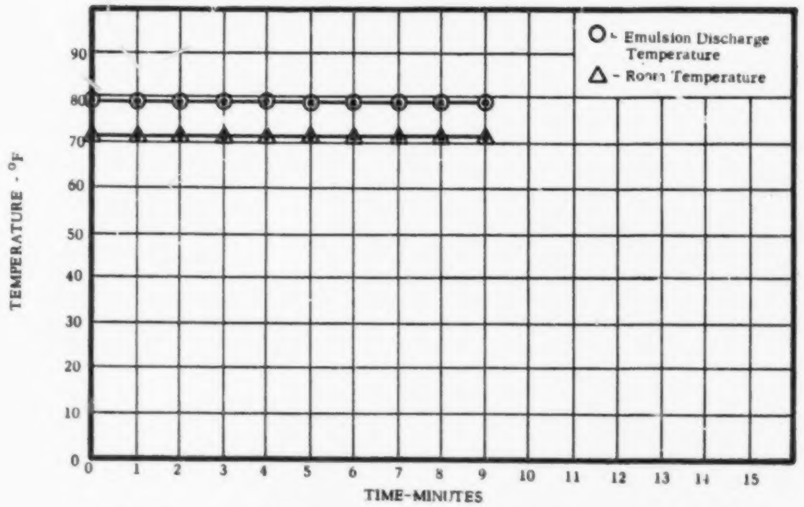


FIGURE 5-6 ROOM & EMULSION DISCHARGE TEMPERATURES ZUEITINA CRUDE

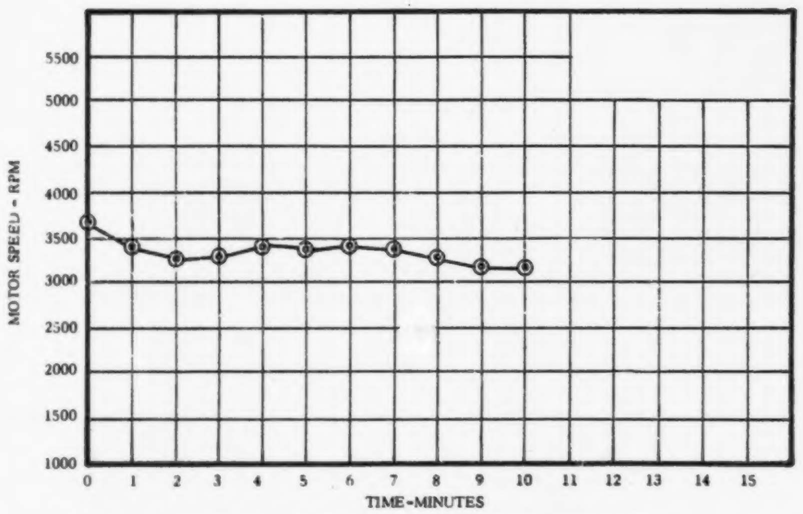


FIGURE 5-7 ZUEITINA CRUDE, BLENDER AIR MOTOR SPEED

TABLE 5-4

EMULSIFICATION PILOT MODEL DATA

TEST RUN NO. 1 - TIA JUANA MEDIUM CRUDE

READING NO.	AIR PRESS MOTOR (psi)	AIR MOTOR SPEED (rpm)	MANIFOLD INLET PRESS (psi)	SEED OUTPUT PRESS (psi)	EMULSION FLOW RATE (l/min)	ROOM TEMP. (°F)	EMULSION DISCHARGE TEMP. (°F)
1	70		34.0	8		75.5	80.0
2	60	3700	33.0	7	7.20	75.5	80.0
3	59	3678	33.0	9	7.00	75.5	80.0
4	54	3540	33.0	10	6.80	75.5	80.0
5	54	2998	33.0	6		75.5	80.0

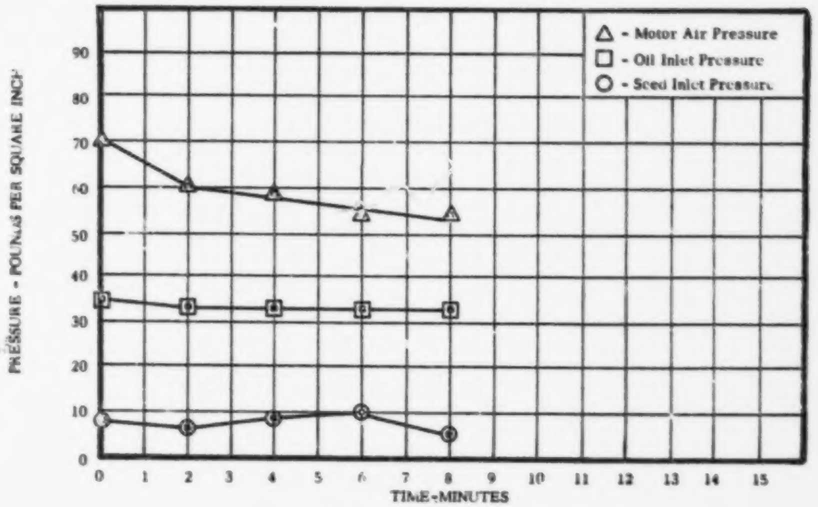


FIGURE 5-8 MIXER MOTOR AIR PRESSURE, OIL & SEED INPUT PRESSURE, RUN NO. 1, TIA JUANA CRUDE

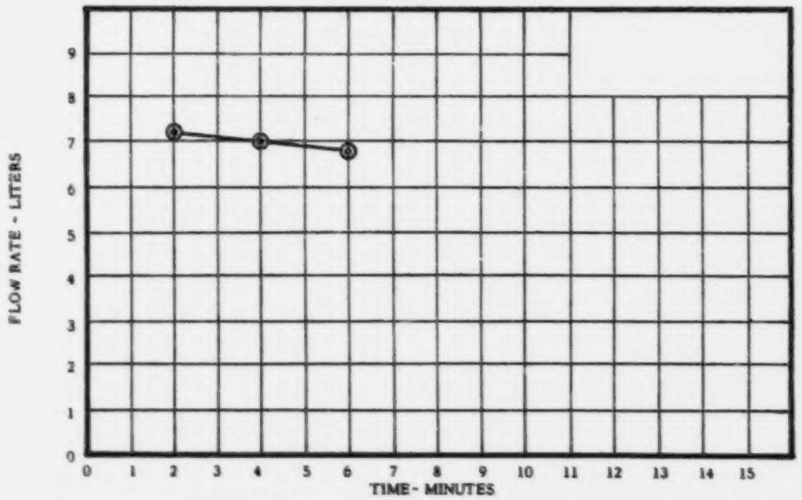


FIGURE 5-9 MEASURED FLOW RATE, RUN NO. 1, TIA JUANA CRUDE

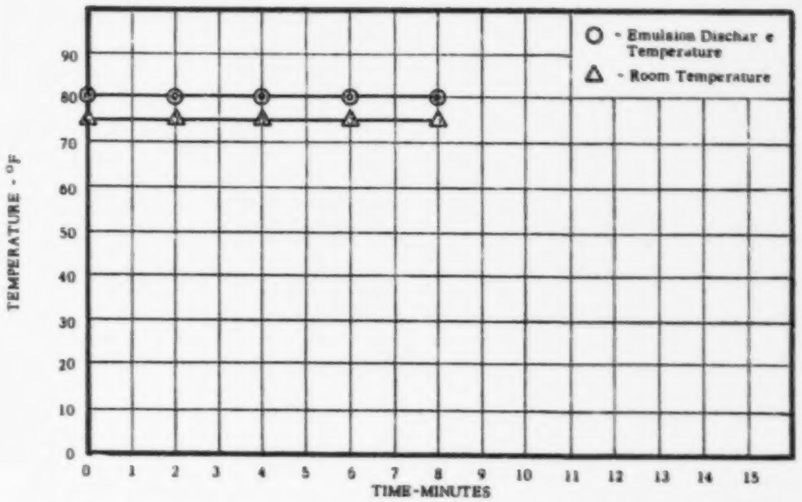


FIGURE 5-10 ROOM & EMULSION DISCHARGE TEMPERATURES, RUN NO. 1, TIA JUANA CRUDE

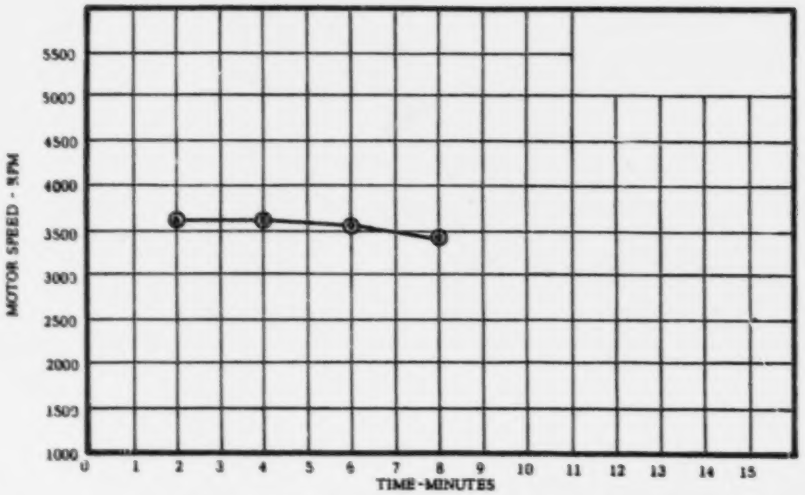


FIGURE 5-11 TIA JUANA CRUDE, RUN NO. 1, BLENDER AIR MOTOR SPEED

TABLE 5-5

EMULSIFICATION PILOT MODEL DATA

TEST RUN NO. 2 - TIA JUANA MEDIUM CRUDE

READING NO.	AIR PRESS MOTOR psi	AIR MOTOR SPEED rpm	MANIFOLD INLET PRESS psi	SEED OUTPUT PRESS psi	EMULSION FLOW RATE l/min.	ROOM TEMP. (^{o}F)	EMULSION DISCHARGE TEMP. (^{o}F)
1	70		32	5	7	80^{o}	72^{o}
2	62	3350	32	4	7	80^{o}	72^{o}
3	60	3250	32	5	7	80^{o}	72^{o}
4	59	3300	32	6	7	80^{o}	72^{o}
5	57	3400	32	6	7	80^{o}	72^{o}
6	54	3350	32	5	7	80^{o}	72^{o}
7	52	3400	32	5	7	80^{o}	72^{o}
8	50	3200	32	5	7	80^{o}	72^{o}
9	50	3180	32	5	7	80^{o}	72^{o}
10	48	3150	32	5	7	80^{o}	72^{o}

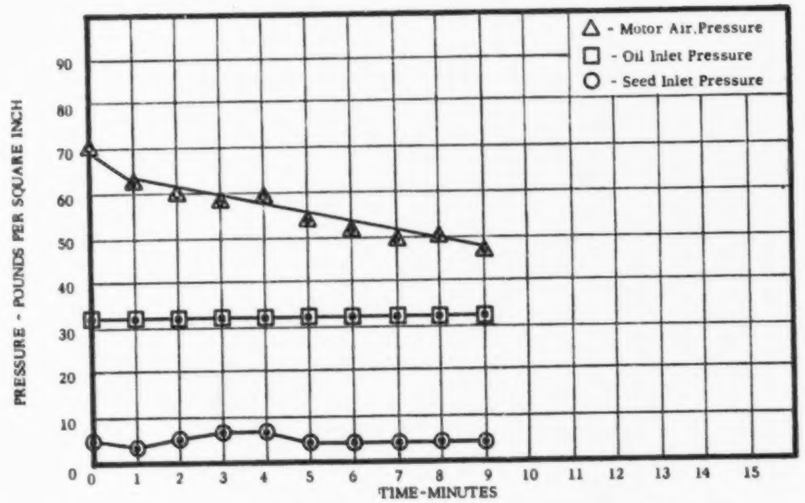


FIGURE 5-12 MIXER MOTOR AIR PRESSURE, OIL & SEED INLET PRESSURES, RUN NO. 2, TIA JUANA CRUDE

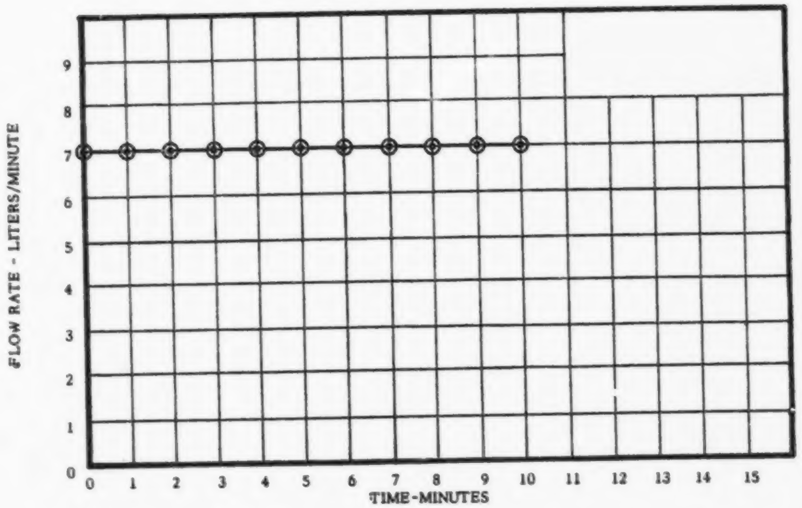


FIGURE 5-13 MEASURED FLOW RATE, RUN NO. 2, TIA JUANA CRUDE

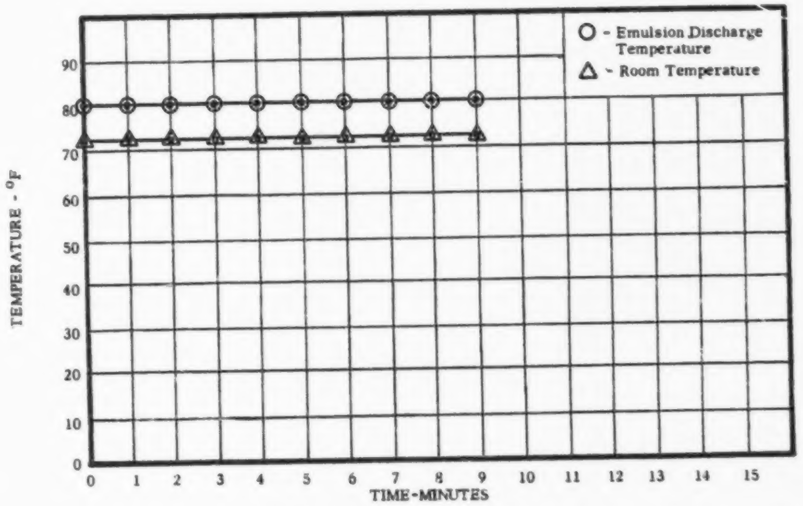


FIGURE 5-14 ROOM & EMULSION DISCHARGE TEMPERATURES, RUN NO. 2, TIA JUANA CRUDE

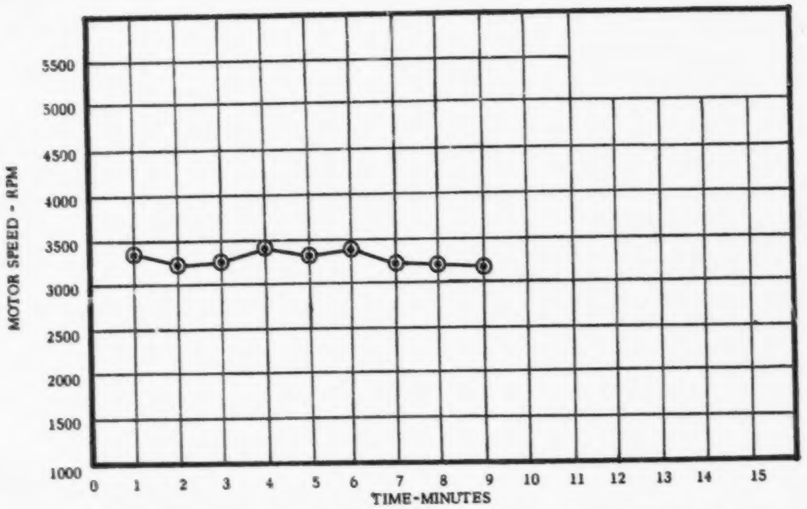


FIGURE 5-15 RUN NO. 2, TIA JUANA CRUDE, BLENDER AIR MOTOR SPEED

TABLE 5-6

EMULSIFICATION PILOT MODEL DATA

TEST RUN NO. 3 - TIA JUANA MEDIUM CRUDE

READING NO.	AIR PRESS MOTOR psi	AIR MOTOR SPEED rpm	MANIFOLD INLET PRESS psi	SEED OUTPUT PRESS psi	EMULSION FLOW RATE l/min.	ROOM TEMP. (°F)	EMULSION DISCHARGE TEMP. (°F)
1	—	—	35.0	5	7.20	74.0	78.0
2	68	—	34.0	4	7.00	74.0	78.0
3	65	—	33.0	3	7.00	74.0	78.0
4	64	—	33.0	4	7.00	74.0	78.0
5	60	—	33.0	5	7.00	74.0	78.0

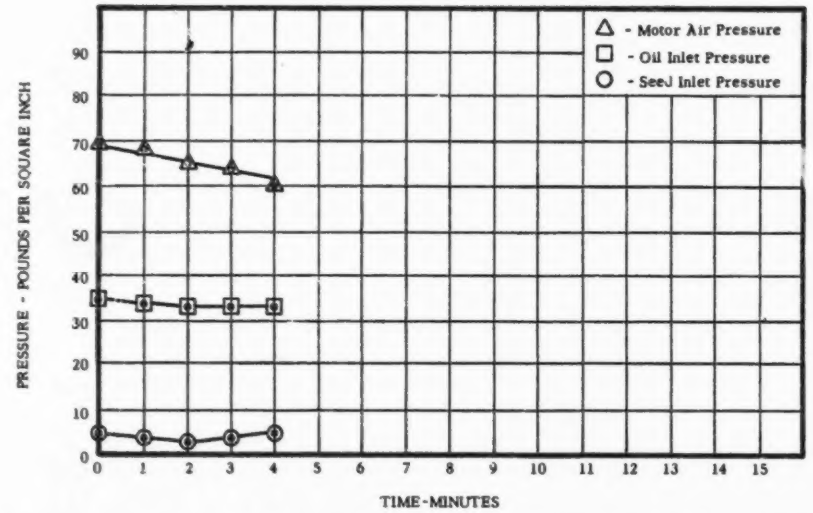


FIGURE 5-16 MIXER MOTOR AIR PRESSURE, OIL & SEED INLET PRESSURE, RUN #3, TIA JUANA CRUDE

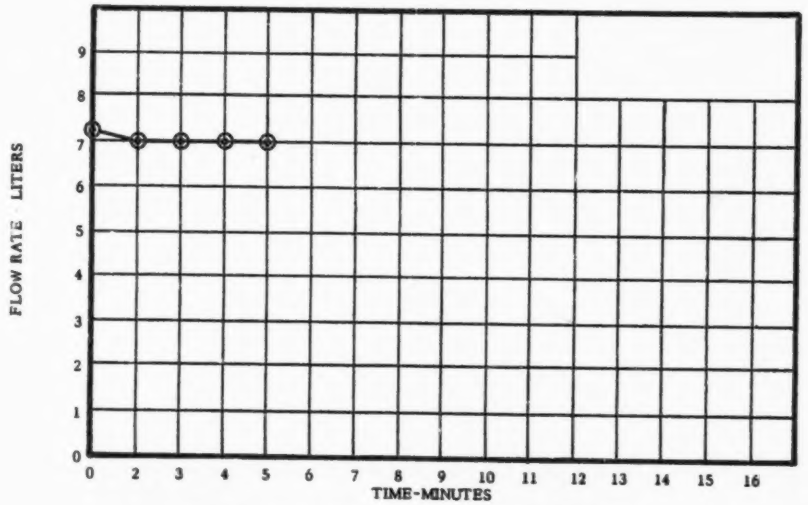


FIGURE 5-17 MEASURED FLOW RATE, RUN #3, TIA JUANA CRUDE

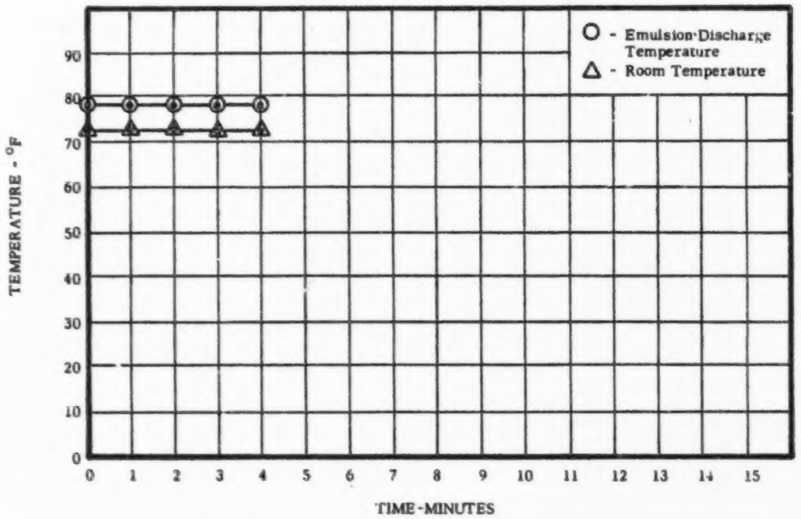


FIGURE 5-18 ROOM & EMULSION DISCHARGE TEMPERATURES, RUN #3, TIA JUANA CRUDE

TABLE 5-7

EMULSIFICATION PILOT MODEL DATA

TEST RUN - NO. 6 FUEL OIL

READING NO.	AIR PRESS MOTOR PSI	AIR MOTOR RPM	MANIFOLD INLET PRESS PSI	SEED OUTPUT PRESS PSI	EMULSION FLOW RATE LITERS/MIN	ROOM TEMP. (°F)	EMULSION DISCHARGE TEMP. (°F)
1	65	3164	56.0	11	—	75	84
2	64	2792	56.0	6	—	75	85
3	65	2569	56.0	12	—	75	87
4	64	2649	56.0	6	3.0	75	87
5	60	2716	56.0	7	—	75	87
6	58	2687	56.0	8	3.0	75	87
7	56	2643	56.0	9	—	75	87
8	54	2508	56.0	11	—	75	87
9	50	2419	56.0	9	3.0	75	87
10	49	2280	56.0	5	—	75	87
11	47	2398	56.0	7	—	75	87
12	45	2358	56.0	10	—	75	87
13	43	2456	56.0	8	3.0	75	87

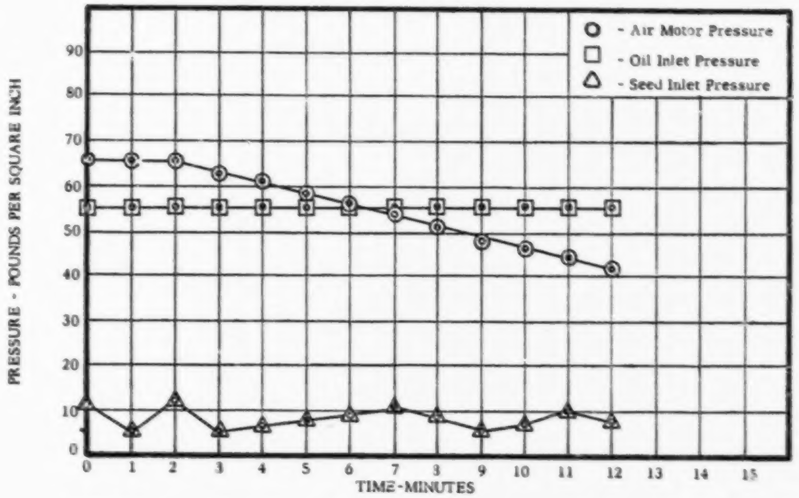


FIGURE 5-19 MIXER MOTOR AIR PRESSURE, OIL & SEED INPUT PRESSURES #6 FUEL OIL

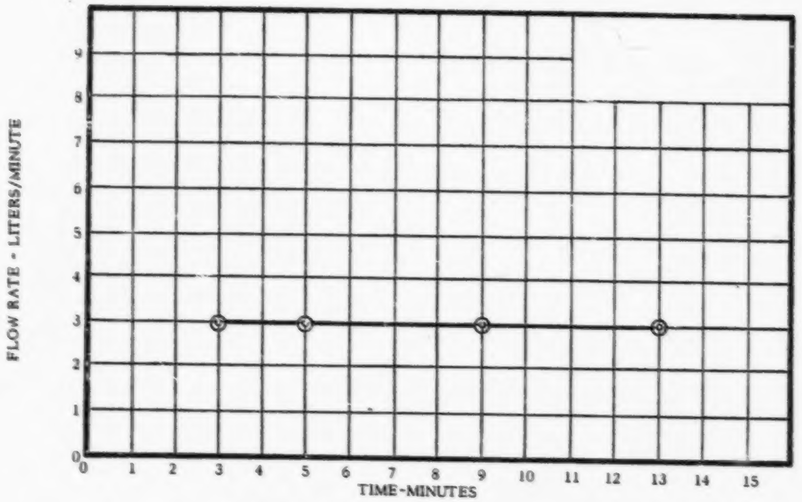


FIGURE 5-20 MEASURED FLOW RATE #6 FUEL OIL

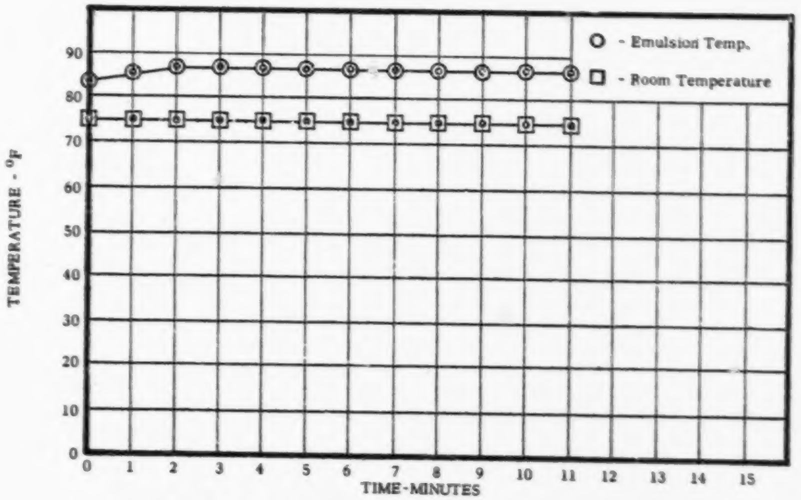


FIGURE 5-21 ROOM & EMULSION DISCHARGE TEMPERATURES #6 FUEL OIL

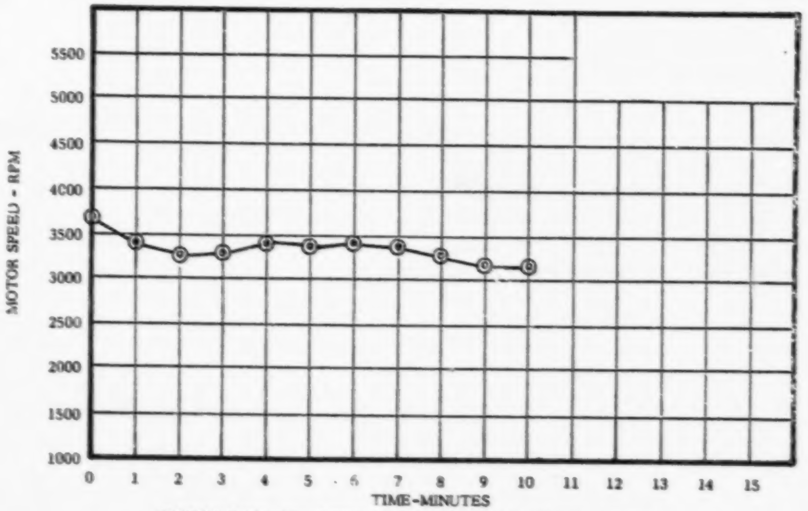


FIGURE 5-22 NO. 6 FUEL OIL, BLENDER AIR MOTOR SPEED

TABLE 5-8

EMULSIFICATION PILOT MODEL DATA

TEST RUN - NO. 2 DIESEL FUEL

READING NO.	AIR PRESS MOTOR PSI	AIR MOTOR RPM	MANIFOLD INLET PRESS PSI	SEED OUTPUT PRESS PSI	EMULSION FLOW RATE LITERS/MIN	ROOM TEMP. (°F)	EMULSION DISCHARGE TEMP. (°F)
1	46	2956	41	2.0	15.00	74	78
2	44	2857	41	1.0	9.23	74	78
3	42	2673	41	5.0	9.23	74	78
4	41	2696	41	5.0	9.23	74	78
5	40	2685	43	5.0	9.23	74	78
6	39	2673	45	5.0	9.23	74	78
7	38	2639	45	5.0	9.23	74	78
8	37	2544	45	5.0	9.16	74	78
9	36	2568	45	4.0	9.23	74	78
10	35	2565	45	4.0	9.23	74	78
11	35	2538	45	4.0	8.57	74	78
12	34	2543	45	3.5	8.57	74	78

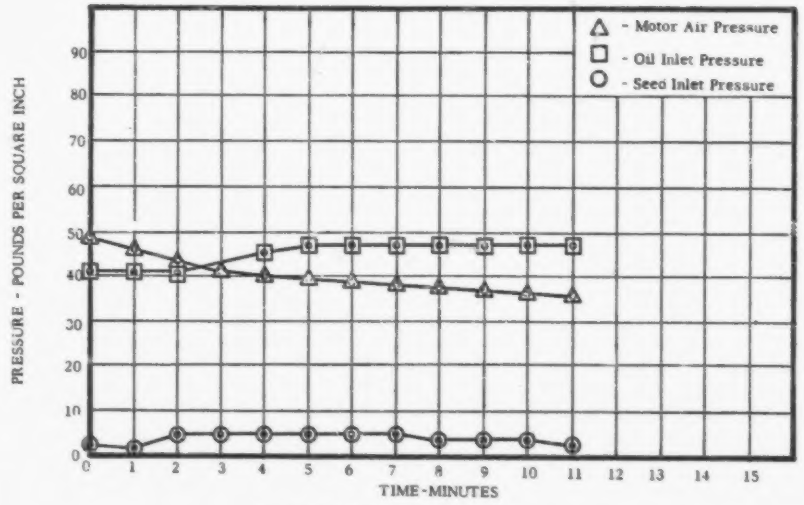


FIGURE 5-23 RUN NO. 1, #2 DIESEL FUEL

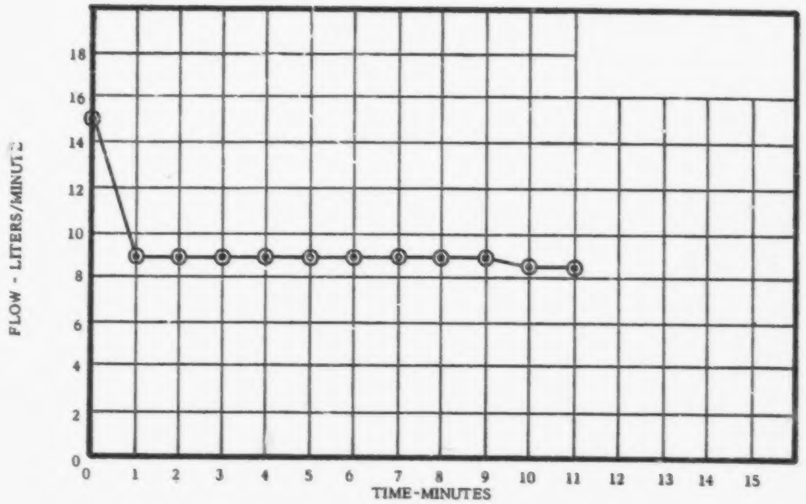


FIGURE 5-24 RUN NO. 1, #2 DIESEL FUEL

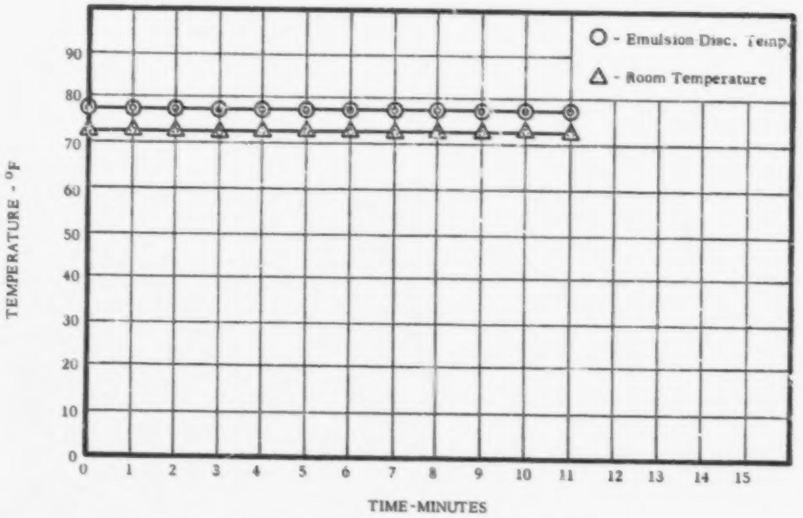


FIGURE 5-25 RUN #1, NO. 2 DIESEL FUEL

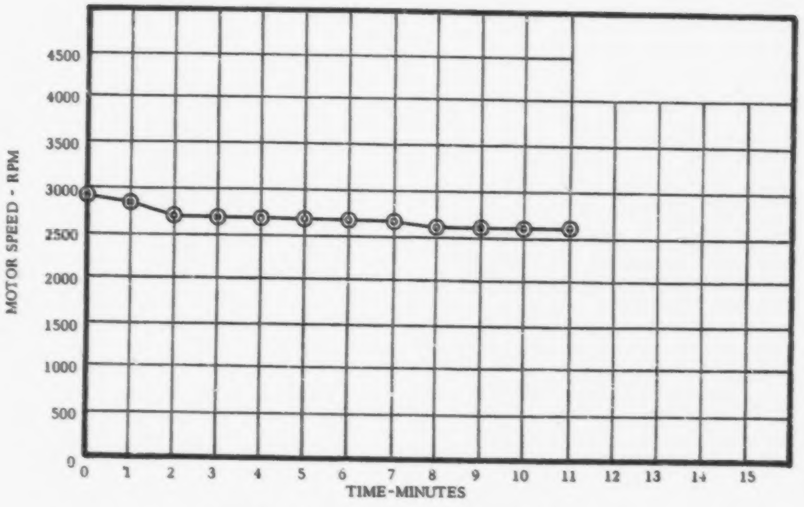


FIGURE 5-26 RUN NO. 1, #2 DIESEL FUEL

that the operation of the emulsification system was consistent for a broad range of oil characteristics. The only significant variation was the flow rate through the blender. The highest flow rate (slightly over 6 gal/min) was obtained with #2 Diesel Fuel during a nonrecorded run. The Zueitina crude oil could be run at nearly the same rate. The flow rate of the viscous #6 Fuel Oil was the lowest at 0.8 gpm.

6. SYSTEM CONCEPTUAL DESIGN

6.1 Emulsification Unit Scale-up to Basic 100-Barrels-Per-Minute Unit

Based on the performance of the bench scale emulsification system, a basic unit capable of producing 100 BPM of emulsion was designed. Figure 6-1 is a plan view and Figure 6-2 an elevation of the basic 100 BPM emulsification unit. Table 6-1 is the parts list for the 100 BPM unit. The basic 100 BPM unit was designed as a complete, skid mounted unit capable of being placed on line as a single unit or in parallel as a module of a multi-unit system. The 100 BPM emulsification unit was designed to operate in the same manner as the bench scale unit described in Section 5.

The oil, treated water and emulsifier are each piped into the emulsification unit through inlets on the left end of the skid. Oil flows through the inlet at the rate of 97 percent of the emulsion discharge flow rate. As the oil enters the line to the inlet manifold, 7 percent is diverted to the seed premix unit through a flow control valve. The remaining 90 percent is distributed by the inlet manifold at the rates shown in Table 6-2. The treated water enters the oil line to the premix unit through a flow control valve at the inlet. The emulsifier inlet is connected to metering pumps which inject the emulsifier into the water stream prior to its connection to the premix oil stream. The combined stream of oil, water and emulsifier then flows through the premix unit where a coarse oil-in-water emulsion is formed. The premixed emulsion then passes over the flat plate, ultrasonic homogenizer where intense cavitation ruptures the coarse emulsion to form a fine, uniform "emulsion seed". The finished "emulsion seed" is pumped from the ultrasonic homogenizer through a check valve to the base inlet of the blending column where the bulk of the oil is blended into the "emulsion seed" to provide the finished 97 percent oil-in-water emulsion.

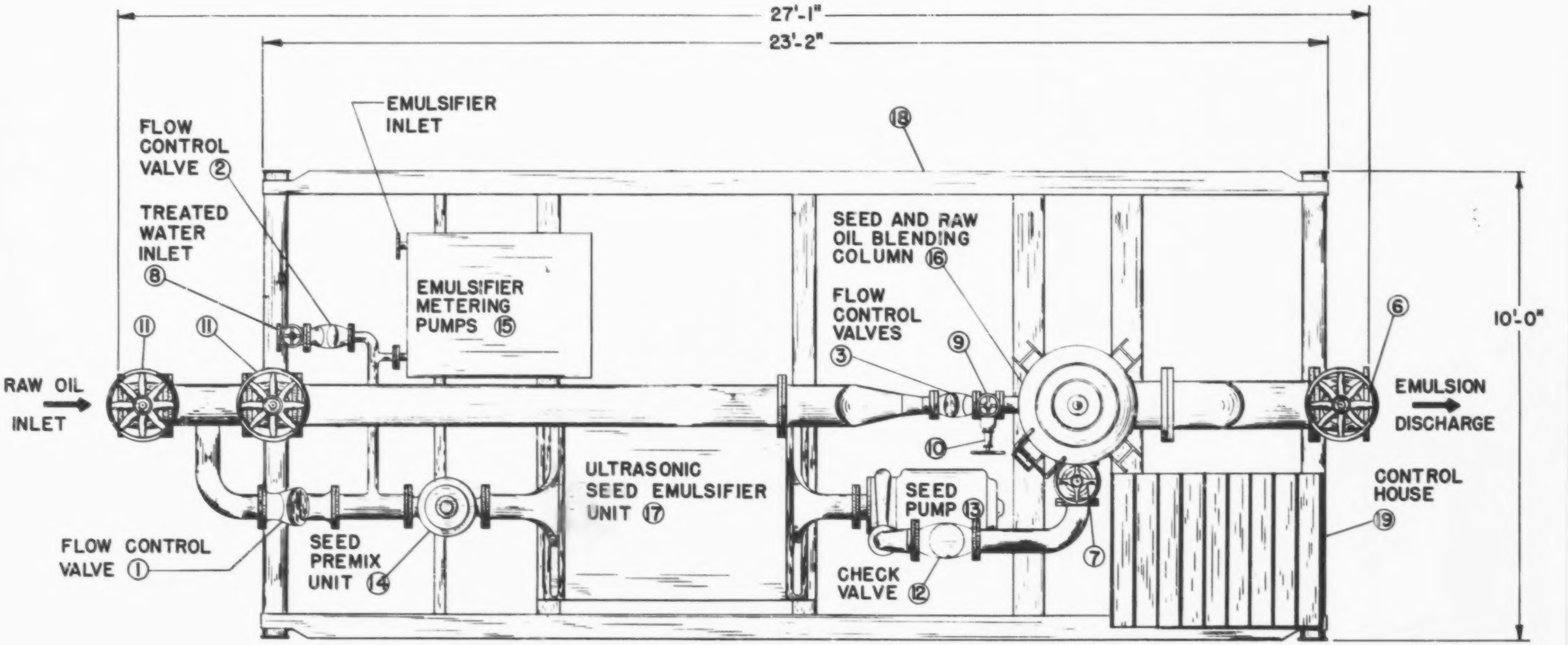
The basic 100 BPM emulsification unit is 27'-1" long by 27'-7" high and is mounted on a 10' by 23'-2" skid. The unit weight is approximately ten tons.

Manual gate valves are specified for use in the unit, but no problem would be encountered in converting to remote control or programmed automatic valves. The system lends itself to complete automation.

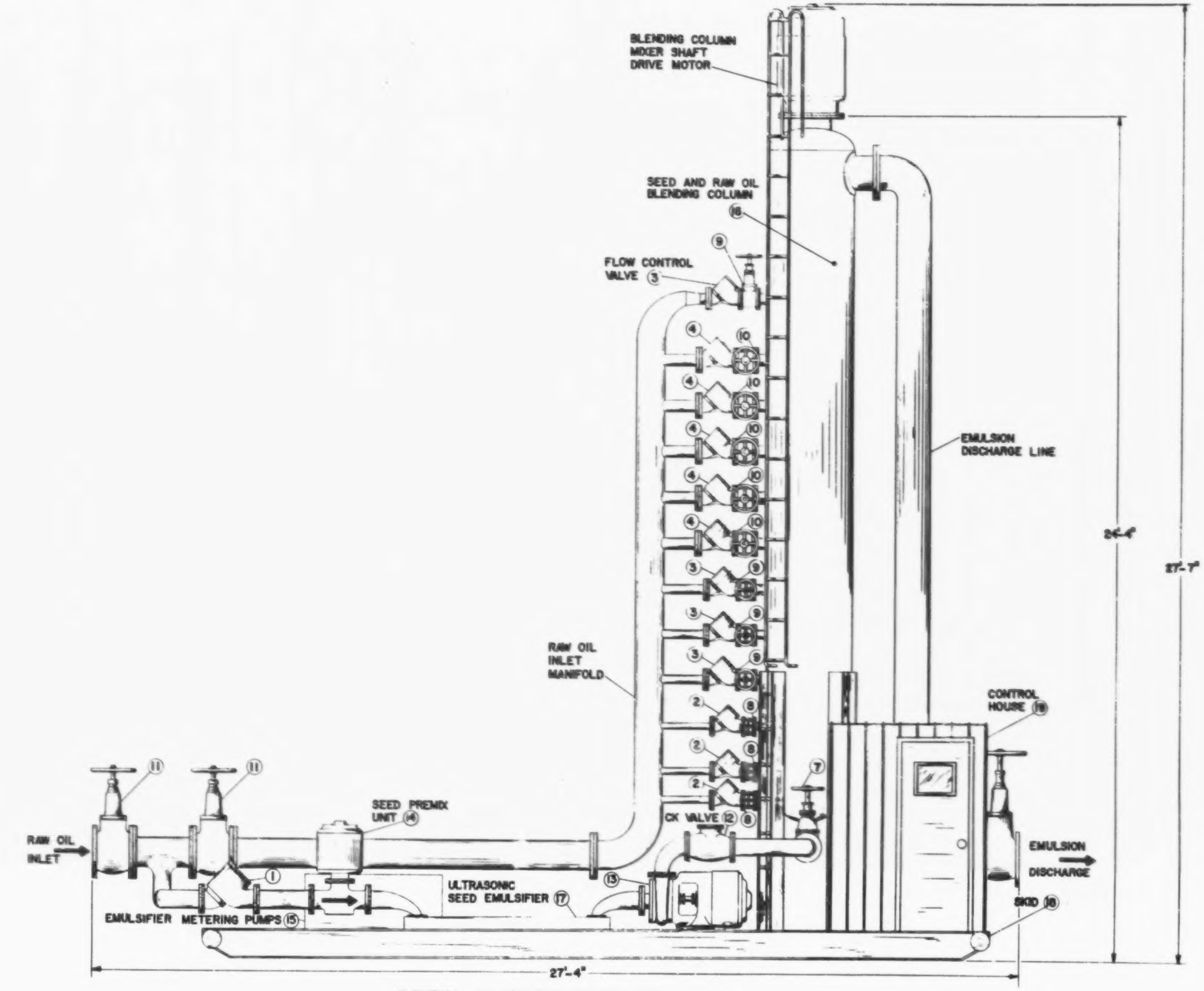
The blender column is powered by a 75 hp electric motor, the premix column by a 5 hp motor and the "emulsion seed" column by a 15 hp motor. The homogenizer is a 100 hp unit.

6.2 Concept of Complete Emulsification System

The basic 100 BPM emulsification unit was designed for use in a single unit system


27'-1"
23'-2"
10'-0"
EMULSIFIER INLET
FLOW CONTROL VALVE ②
TREATED WATER INLET ⑧
⑪
⑪
RAW OIL INLET
EMULSIFIER METERING PUMPS ⑮
⑱
SEED AND RAW OIL BLENDING COLUMN ⑯
FLOW CONTROL VALVES
③
⑨
⑩
⑥
EMULSION DISCHARGE
ULTRASONIC SEED EMULSIFIER UNIT ⑰
SEED PUMP ⑬
CONTROL HOUSE ⑲
⑦
CHECK VALVE ⑫
FLOW CONTROL VALVE ①
SEED PREMIX UNIT ⑭

PLAN VIEW - 100 BPM EMULSIFICATION UNIT


BLENDING COLUMN
MIXER SHAFT
DRIVE MOTOR
SEED AND RAW OIL
BLENDING COLUMN ⑯
FLOW CONTROL
VALVE ③
⑨
④
⑩
③
⑧
②
RAW OIL
INLET
MANIFOLD
EMULSION
DISCHARGE LINE
CONTROL
HOUSE ⑲
⑦
CK VALVE ⑫
⑪
SEED PREMIX
UNIT ⑭
RAW OIL
INLET
①
⑬
ULTRASONIC
SEED EMULSIFIER ⑰
EMULSIFIER METERING PUMPS ⑮
SKID ⑱
EMULSION
DISCHARGE
24'-4"
27'-7"
27'-4"

ELEVATION—100 BPM EMULSIFICATION UNIT

TABLE 6-1

BASIC 100 BPM EMULSIFICATION UNIT PARTS LIST

ITEM NO.	QUANTITY REQUIRED	DESCRIPTION	WEIGHT EACH (pounds)	WEIGHT TOTAL (pounds)
1	1	7505780 Rockwell Control Valve	175	175
2	4	2" MDL 780 Rockwell Control Val.	60	240
3	4	3" MDL 780 Rockwell Control Val.	96	384
4	5	4" MDL 780 Rockwell Control Val.	135	675
5	1	702 Rockwell Check Value	200	200
6	1	12" Gate Valve 150 psi	653	653
7	1	6" Gate Valve 150 psi	179	179
8	4	2" Gate Valve 150 psi	40	160
9	4	3" Gate Valve 150 psi	64	256
10	5	4" Gate Valve 150 psi	107	535
11	2	10" Gate Valve 150 psi	475	950
12	1	6" Swing Check Valve	172	172
13	1	4 x 5 Centrifugal Pump & Motor	615	615
14	1	In Line Mixer	940	940
15	1	Emulsion Metering Pumps	900	900
16	1	Blending Column	5, 050	5, 050
17	1	Ultrasonic Transducer (assembly)	1, 500	1, 500
18	1	Skid	5, 000	5, 000
19	1	Control House	800	800
20	8	Ultrasonic Generator	200	1, 600
21	1	12" MDL 702 Rockwell Control Valve	175	175
		TOTAL		21, 159

TABLE 6-2

BASIC 100 BPM EMULSIFICATION UNIT

OIL FLOW RATE INTO BLENDING COLUMN

INLET NO.	% of 90 BPM FLOW THRU INLET	FLOW RATE (bbl/min)	FLOW RATE (gal/min)
1	1	0.9	37.8
2	2	1.8	75.6
3	3	2.7	113.4
4	5	4.2	176.4
5	7	6.3	264.6
6	10	8.4	352.8
7	11	9.9	415.8
8	12	11.2	470.4
9	12	12.0	504.2
10	13	12.4	520.8
11	14	12.1	508.2
12	10	8.1	340.0

or for parallel installation as required to meet the demands of a multi-unit system. Figure 6-3 is a schematic of a single unit crude oil emulsification system. The system consists of the basic 100 BPM emulsification unit, an oil storage battery (a pipe line could replace the oil storage battery), a water storage tank (a water supply line could be used) and an emulsifier storage tank. A means of transferring the stored liquids to the emulsification unit is also required. The pressure in the unit forces the oil into the ship without further pumping.

Figure 6-4 is a schematic drawing of a multi-unit emulsification system. Each of the basic 100 BPM units is represented by a block labeled "emulsification unit".

These units are parallel manifolded to the tanker loading lines on the discharge side and to the oil, water and emulsifier supply systems on the inlet side.

If a large volume of one petroleum product was handled at a terminal facility, several units would be placed on site. If the peak demand at such a terminal was 600 BPM, six units would be employed as shown in Figure 6-4.

Table 6-3 gives the required loading time for barges and tankers with cargo capacities from 1,000 through 200,000 tons, relative to the number of emulsification units, for one through seven 100 BPM units. For example, if a tanker with a capacity of 110,000 tons (approximately the size of the Torrey Canyon) used six units to accomplish onloading, approximately 23 hours would be required. If the same tanker was allowed 36 hours for onloading, only four units would be required.

6.3 Placement of Emulsification System

A visit to typical Gulf Coast terminals revealed that there is insufficient dockside space to allow installation of one or more emulsification units. It would be necessary to install the emulsification units where space was available and pipe the finished emulsion to the dock.

One or more of the emulsification units could be mounted on a barge for use at offshore terminals and offshore production facilities.

Placement of the emulsification units is not critical. If necessary they could be located away from the loading terminal, or they could be on the tanker deck.

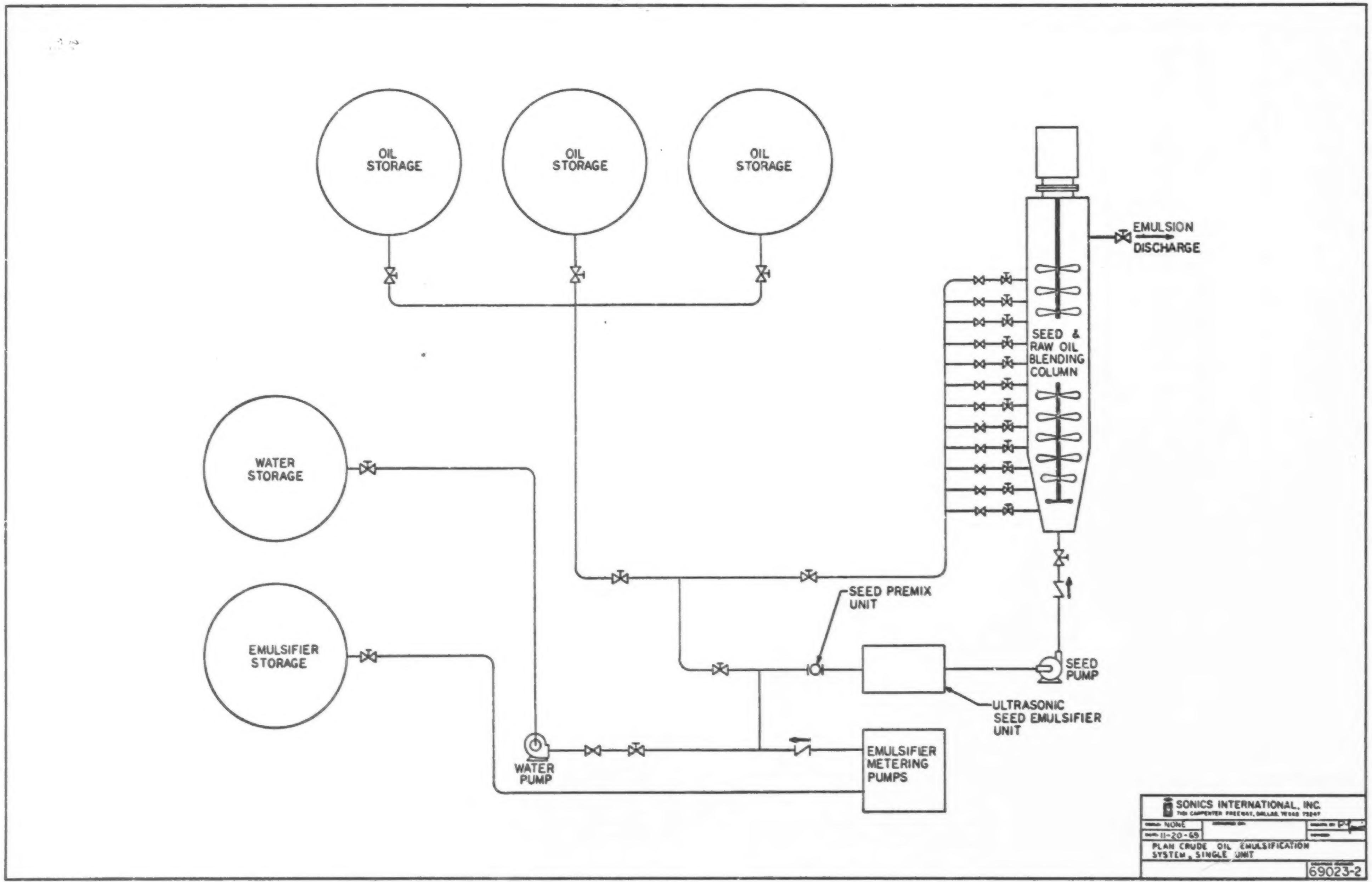

OIL STORAGE
OIL STORAGE
OIL STORAGE
EMULSION DISCHARGE
SEED & RAW OIL BLENDING COLUMN
WATER STORAGE
EMULSIFIER STORAGE
SEED PREMIX UNIT
SEED PUMP
ULTRASONIC SEED EMULSIFIER UNIT
WATER PUMP
EMULSIFIER METERING PUMPS
SONICS INTERNATIONAL, INC.
NONE
11-20-69
PLAN CRUDE OIL EMULSIFICATION SYSTEM, SINGLE UNIT
69023-2

FIGURE 6-3 SINGLE UNIT CRUDE OIL EMULSIFICATION SYSTEM

TABLE 6-3 TIME REQUIRED TO LOAD A TANKER WITH 100 BPM UNITS

TANKER CAPACITY 1000 TONS	TANKER CAPACITY 1000 BBLS	1 UNIT HOURS	2 UNITS HOURS	3 UNITS HOURS	4 UNITS HOURS	5 UNITS HOURS	6 UNITS HOURS	7 UNITS HOURS
1	7.5	1.25						
2	15.0	2.50						
3	22.5	3.75						
4	30.0	5.00						
5	37.5	6.25						
6	45.0	7.50						
7	52.5	8.75	4.38					
8	60.0	10.00	5.00					
9	67.5	11.25	5.62					
10	75.0	12.50	6.25	4.10				
20	150.0	25.00	12.50	8.20	6.15			
30	225.0	37.50	18.75	12.30	9.36	7.50	6.15	
40	300.0	50.00	25.00	16.40	12.30	10.00	8.20	7.15
50	375.0	62.50	31.25	20.50	15.62	12.30	10.41	8.91
60	450.0	75.00	37.50	25.00	18.45	15.00	12.50	10.70
70	525.0	87.50	43.75	29.10	21.86	17.30	14.58	12.50
80	600.0	100.00	50.00	33.20	25.00	20.00	16.66	14.28
90	675.0	112.50	56.25	37.30	28.70	22.30	18.75	16.06
100	750.0	125.00	62.50	41.40	31.15	25.00	20.83	17.85
110	825.0	137.50	68.75	45.50	34.22	27.30	22.91	19.63
120	900.0	150.00	75.00	50.00	37.30	30.00	25.00	21.41
130	975.0	162.50	81.25	54.10	40.37	32.30	27.08	23.20
140	1,050.0	175.00	87.50	58.20	43.45	35.00	29.16	25.00
150	1,125.0	187.50	93.75	62.30	46.52	37.30	31.25	26.78
160	1,200.0	200.00	100.00	66.40	50.00	40.00	33.33	28.56
170	1,275.0	212.50	106.25	70.50	53.70	42.30	35.41	30.35
180	1,350.0	225.00	112.50	75.00	56.15	45.00	37.50	32.13
190	1,425.0	237.50	118.75	79.10	59.22	47.30	39.58	33.91
200	1,500.0	250.00	125.00	83.20	62.30	50.00	41.66	35.70

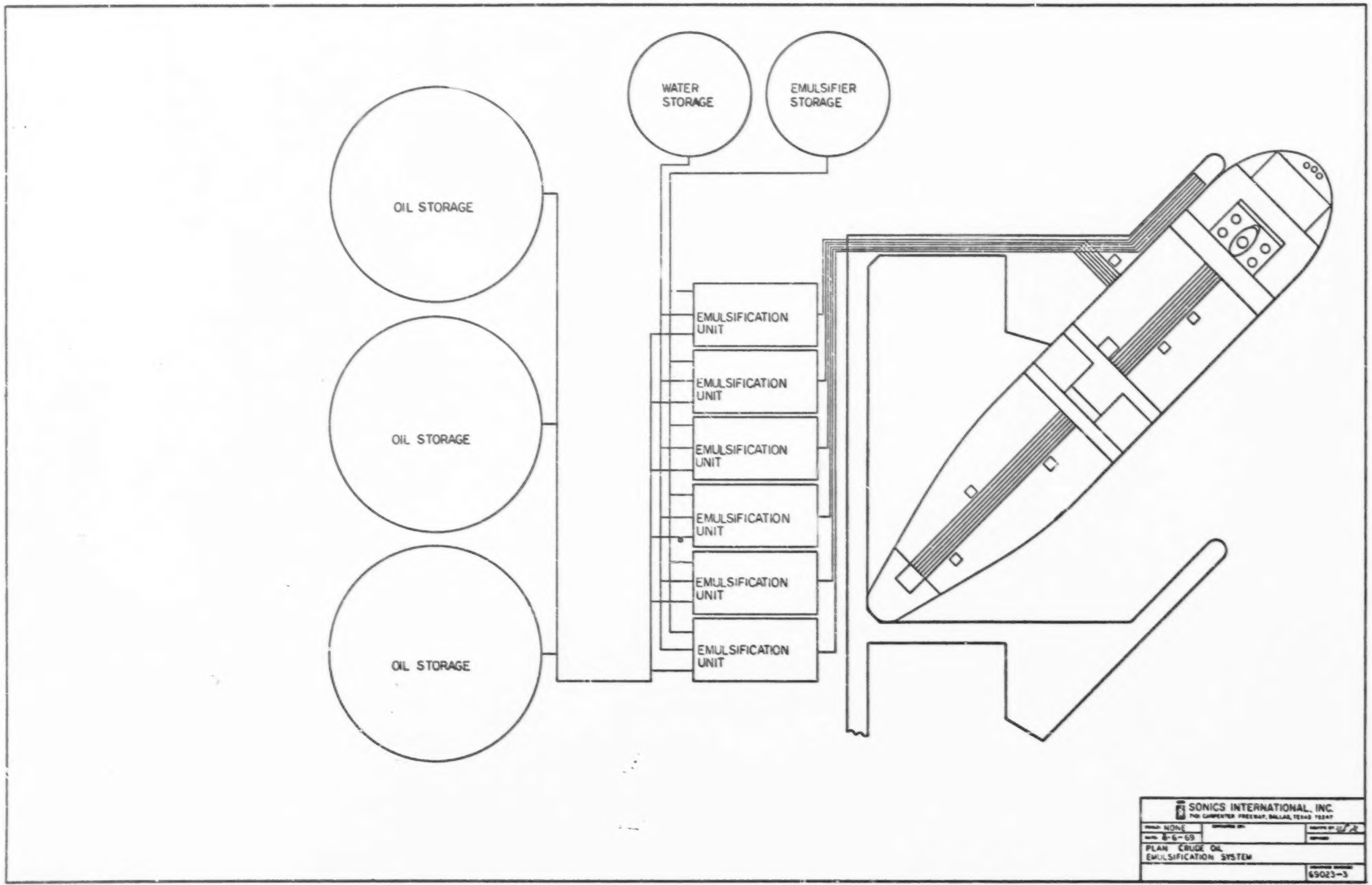

WATER STORAGE
EMULSIFIER STORAGE
OIL STORAGE
OIL STORAGE
OIL STORAGE
EMULSIFICATION UNIT
EMULSIFICATION UNIT
EMULSIFICATION UNIT
EMULSIFICATION UNIT
EMULSIFICATION UNIT
EMULSIFICATION UNIT
SONICS INTERNATIONAL, INC.
NONE
8-6-69
PLAN CRUDE OIL
EMULSIFICATION SYSTEM
65023-3

FIGURE 6-4 MULTI-UNIT CRUDE OIL EMULSIFICATION SYSTEM

7. ECONOMICS OF EMULSIFICATION PROCESS

7.1 Introduction

Considerable effort was spent in this study in attempts to obtain representative numbers necessary for a complete economic analysis. Estimates of capital costs for the equipment and operating cost for the total system are relatively good. Chemical emulsifier costs are not exact since costs vary with composition. Optimums of emulsifiers were beyond the scope of this study. All of the numbers required to assess "cost offsets" were not available, primarily because of the competitive nature of those phases of the business and vagueness of numbers available in some cases.

From the standpoint of economics, it would be desirable to have the additional cost of a system to emulsify oil for transportation not exceed the savings that would result from its use. However, under present conditions with our Country's all-out efforts to eliminate pollution problems, it is difficult to fix dollar magnitudes on incentives for control of oil spills. To the degree these factors become significant, the total economic picture is not seen from the cost estimates developed in this report.

Tankers vary in size so much that "typical" or "average" are meaningless as tanker capacity descriptions. The World Wide Tanker Nominal Scale indicates a "standard vessel" for rate calculations for 1969 would be as follows:

Summer deadweight	19,500 tons
Summer draft laden in salt water	30' 60"
Average service speed	14 knots
Fuel consumption at sea	28 tons per day
Fuel consumption in port	5 tons per day
Port time allowance	96 hours
Fixed time element	$1,800 per day
Brokerage	$2,500

The trend in tanker size is rapidly toward the super tankers. These huge vessels, 100,000 deadweight tons and larger, now constitute less than 10 percent of the world's tanker fleet, but are projected to represent 50 percent by 1975. Two sizes have been selected as examples for this section of the report: 1) 20,000 tons (approximate "standard vessel") and 2) 200,000 tons (representative of super tanker).

7.2 Cost of Emulsified System for Oil Transportation

7.2.1 Loading Rate Considerations

Tanker rental rates are high, even when in port for loading. World Wide Tanker Nominal Scale, a schedule intended as a standard reference by which rates for all voyages and market levels can be prepared, fixes demurrages for a 100,000 summer deadweight ton tanker is $13,200 per day. Laytime allowances for loading and discharging are set at 72 hours. From this it is seen that loading rates become important in selecting size of units for the conceptual design. Processing rates, available through single unit or multiple unit stations, must be comparable to conventional loading rates of present facilities. The basic unit selected for the concept presented in this study is capable of operating at 100 BPM or 144,000 BPD. A loading timetable for units of this size is shown in Table 6.3. In Table 6.3, "Tons" are long tons and equal to 2,240 pounds or 7.5 barrels.

7.2.2 Capital Costs of Equipment

The concept presented in this study contemplates a system which uses the present lines, pumps and docking facilities with the addition of multiple skid mounted emulsification units to be located on or near the present docks. The emulsion, when formed, would flow through conventional loading lines in the usual "plug flow" of slippery gelled materials. Costs per single 100 BPM unit are outlined on Table 7.2-1. Outlined costs total $84,000 per unit, however, with a contingency for unidentified miscellaneous costs, the full cost of a single unit is estimated at $100,000.

7.2.3 Operating Costs of System

Estimates of operating costs for the system are shown on Table 7.2-2. Since several of the cost items included vary with the number of units at a location and the volume handled for a period of time, two sample cases were used to determine costs per barrel:

Case I - 20,000 ton tanker with 1 - 100 BPM unit operating 60 percent of time and 1 - 100 BPM unit on stand-by.

Case II - 200,000 ton tanker with 6 - 100 BPM units operating 80 percent of time with 1 - 100 BPM unit on stand-by.

Estimates of costs range from 1.58 cents per barrel for Case II to 4.32 cents per barrel for Case I. These numbers are the operating costs for the emulsification units only and are exclusive of chemical and break-back costs.

7.2.4 Cost of Chemical Emulsifier

Costs of chemicals used in the experimental portions of this study would be prohibitive (estimates range from $0.37 to $0.50 per pound or $0.67 to $0.92 per barrel processed) for a full scale operation. However, optimums of cost and performance of emulsifier were beyond the scope of this study. In large volumes,

TABLE 7.2-1

BASIC 100 BPM EMULSIFICATION UNIT COST ESTIMATE

ITEM NO.	QUANTITY REQUIRED	DESCRIPTION	COST EACH (dollars)	COST TOTAL (dollars)
1	1	7505780 Rockwell Control Valve	681.00	681.00
2	4	2" MDL 780 Rockwell Control Val.	367.00	1,468.00
3	4	3" MDL 780 Rockwell Control Val.	456.00	1,824.00
4	5	4" MDL 780 Rockwell Control Val.	598.00	2,996.00
5	1	702 Rockwell Check Value	2,481.00	2,481.00
6	1	12" Gate Valve 150 psi	540.00	540.00
7	1	6" Gate Valve 150 psi	136.50	136.50
8	4	2" Gate Valve 150 psi	47.70	190.80
9	4	3" Gate Valve 150 psi	62.60	250.40
10	5	4" Gate Valve 150 psi	86.00	430.00
11	2	10" Gate Valve 150 psi	390.00	780.00
12	1	6" Swing Check Valve	137.00	137.00
13	1	4 x 5 Centrifugal Pump & Motor	1,381.00	1,381.00
14	1	In Line Mixer	1,922.00	1,922.00
15	1	Emulsion Metering Pumps	3,198.00	3,198.00
16	1	Blending Column	9,270.00	9,270.00
17	1	Ultrasonic Transducer (assembly)	4,000.00	4,000.00
18	1	Skid	1,440.00	1,440.00
19	1	Control House	1,200.00	1,200.00
20	8	Ultrasonic Generator	4,200.00	4,200.00
21	1	12" MDL 702 Rockwell Control Valve	2,073.00	2,073.00
22	1	Manufacture and Assembly Estimate	13,900.00	13,900.00
		TOTAL:		83,848.00

TABLE 7.2-2

EMULSIFICATION UNIT COSTS OF OPERATION

Item	Case I 20,000 ton tanker 1-100 BPM Units (M$/Yr)	 (¢/bbl)	Case II 200,000 ton tanker 6-100 BPM Units (M$/Yr)	 (¢/bbl)
* Labor	70	2.90	170	0.90
* Equipment Amortization (10 yr.)	20	0.64	70	0.29
Interest on Investment (20% on balance)	20	0.64	70	0.29
Maintenance	2	0.06	12	0.05
Power	14	0.05	84	0.03
Taxes	1	0.03	6	0.02
Total	147	4.32	462	1.58

	Case I	Case II
Use Factor	0.6	0.8
Terminal Handling Rate (Million barrels per year)	31	245
Costs (¢/bbl)	4.32	1.58

* Case I - Labor at $5/Hr. plus 125 percent overhead for 3 shifts per day.
Case II - Assumes increase in labor proportional to square root increase of capital.

* Assumes basic unit costs of 100 M $ each. Case I includes 1 unit in use 60 percent of time and 1 unit on "stand-by". Case II includes 6 units in use 80 percent of time and 1 unit on "stand-by".

chemicals of the same class as those used in this study should be obtained for about $0.12 per pound or $0.22 per barrel of oil processed. A cost schedule covering a reasonable range of chemical costs for varying tanker capacities is shown on Table 7.2-3.

A volume of water equal to about 2.5 percent of the tanker capacity will be required for processing; however, water costs will be negligible in relation to other costs of the operation.

Emulsions must be broken-back when the refinery is reached. Regular chemical demulsifiers would cost about the same as above, or double the chemical costs for the emulsification/demulsification process.

While these costs appear prohibitive, discussions with chemical suppliers indicate reductions in costs could likely be achieved through development efforts on chemicals for the specific purpose, particularly when considering the potential volumes that would be used.

7.2.5 Possible Gains Offsetting Emulsification Costs

The primary purpose of emulsification would be to reduce potential pollution hazards by spills during emergencies. There would be other possible advantages:

(a) Fire hazards would be greatly reduced because the emulsion is not an insulator as is oil, and therefore would not build up static charges. Insurance rates should be reduced because of lower hazards.

(b) Any salt present in the crude would go into the water phase. In some cases this would desalt the crude to a level that would not require further treating at the refinery, thus reducing costs up to 5 cents per barrel.

(c) Evaporation rates would be lowered, lessening light fraction loss during transit at sea.

(d) The high viscosity of the emulsion would greatly reduce leakage from the ship through normal small holes and ruptures.

(e) The rapid dispersion of the emulsion in the sea would favor rapid bacterial degradation without damage to sea life or beaches.

7.2.6 Possible Procedure Modifications

It has been our experience that ultrasonic treatment will break an emulsion back to about 90 percent free oil and 10 percent "emulsion seed", the latter

TABLE 7.2-3

SCHEDULE OF EMULSIFIER COSTS

TANKER CAPACITY		EMULSIFIER	COST OF EMULSIFIER FOR GIVEN TANKER CAPACITY						
1000 TONS	1000 BBLS	POUNDS	6¢/lb	9¢/lb	12¢/lb	15¢/lb	18¢/lb	21¢/lb	24¢/lb
			(11¢/bbl)	(16¢/bbl)	(22¢/bbl)	(27¢/bbl)	(33¢/bbl)	(38¢/bbl)	(44¢/bbl)
1	7.5	13,782	$ 826	$1,240	$ 1,653	$ 2,067	$ 2,480	$ 2,894	$ 3,307
2	15.0	27,565	1,653	2,480	3,307	4,134	4,961	5,788	6,615
3	22.5	41,348	2,480	3,721	4,961	6,202	7,442	8,683	9,923
4	30.0	55,131	3,307	4,961	6,615	8,269	9,923	11,577	13,231
5	37.5	68,914	4,134	6,202	8,269	10,337	12,404	14,471	16,539
6	45.0	82,696	4,961	7,442	9,923	12,404	14,885	17,366	19,847
7	52.5	96,479	5,788	8,683	11,577	14,471	17,366	20,260	23,154
8	60.0	110,262	6,615	9,923	13,231	16,539	19,847	23,155	26,462
9	67.5	124,045	7,442	11,164	14,885	18,606	22,328	26,049	29,770
10	75.0	137,828	8,269	12,404	16,539	20,674	24,809	28,943	33,078
20	150.0	275,656	16,539	24,809	33,078	41,348	49,618	57,887	66,157
30	225.0	413,484	24,809	37,213	49,618	62,022	74,427	86,831	99,236
40	300.0	551,313	33,078	49,618	66,157	82,696	99,236	115,775	132,315
50	375.0	689,141	41,348	62,022	82,696	103,371	124,045	144,719	165,393
60	450.0	826,969	49,618	74,427	99,236	124,045	148,854	173,663	198,472
70	525.0	964,797	57,887	86,831	115,775	144,719	173,663	202,607	231,551
80	600.0	1,102,626	66,157	99,236	132,315	165,393	198,472	231,551	264,630
90	675.0	1,240,454	74,427	111,640	148,854	186,068	223,281	260,495	297,708
100	750.0	1,378,282	82,696	124,045	165,393	206,742	248,090	289,439	330,787
110	825.0	1,516,110	90,966	136,449	181,933	227,416	272,899	318,383	363,866
120	900.0	1,653,939	99,236	148,854	198,472	248,090	297,709	347,327	396,945
130	975.0	1,791,767	107,506	161,259	215,012	268,765	322,518	376,271	430,024
140	1,050.0	1,929,595	115,775	173,663	231,551	289,439	347,327	405,214	463,102
150	1,125.0	2,067,423	124,045	186,068	248,090	310,113	372,136	434,158	496,181
160	1,200.0	2,205,252	132,315	198,472	264,630	330,787	396,945	463,102	529,260
170	1,275.0	2,343,080	140,584	210,877	281,169	351,462	421,754	492,046	562,339
180	1,350.0	2,480,908	148,854	223,281	297,708	372,136	446,563	520,990	595,417
190	1,425,0	2,618,736	157,124	235,686	314,248	392,810	471,372	549,934	628,496
200	1,500.0	2,756,565	165,393	248,090	330,787	413,484	496,181	578,878	661,575

consisting of about 30 percent aqueous phase and 70 percent oil. If this operation were installed at the refinery, the 90 percent oil being sent to the refinery and the 10 percent "emulsion seed" being returned with the ship for use with the next oil cargo, the chemical cost would be reduced to capital cost and makeup; but the ship's capacity would be reduced by 7 percent because of the returned oil.

There is indication from the literature that some emulsions can be completely broken back by mechanical means as mentioned in Section 4.8 of this report. If this were possible at a cost similar to the equipment operation cost for emulsification, the picture would be much more attractive.

Estimates of savings for both the above discussed modifications in procedure are included in Table 7.2-4.

7.3 Discussion of Economics of Emulsification Process

Estimates of the economic loss caused by oil spills ranges from 5 to 10 cents per barrel of oil shipped. Emulsification prior to shipment would offer the advantage of causing oil spilled gradually or by catastrophe to become widely dispersed in the sea. It would follow sea currents along shore or seaward instead of following the wind which frequently carries it ashore. Further, as it became increasingly diluted with sea water, it would soon reach the non-toxic level, and would readily be degraded by bacteria.

Estimates of costs for the emulsification/demulsification process for transporting oils are summarized on Table 7.3-1. It can be seen that total processing costs range from about 20 to 83 cents per barrel, without consideration of cost offsets. Cost offsets could reduce these numbers from 5 to 15 cents per barrel. Modifications of the procedure itself could provide additional savings up to nearly 4 cents per barrel. Due to the variation in costs of, and the alternates available in estimating overall costs, a nomograph is included with an example calculation on Figure 7.2-1 of this report.

TABLE 7.3-1

SUMMARY OF COSTS AND POTENTIAL COST REDUCTIONS - RANGE

I. Summary of Costs

Item	Practical Range Low (¢/bbl.)	 High (¢/bbl.)	Notes of Explanation
a) Operating Costs of System	1.58	4.32	Includes amortization of equipment; high value calculated on basis of small tanker (20,000 ton); low value calculated on basis of large tanker (200,000 ton).
b) Chemical (Emulsifier) Costs	16.50	38.50	High value based on chemical cost of 21 cents per pound. Low value based on chemical cost of 12 cents per pound (lowest quote obtained from chemical supplier).
c) Emulsion Break-Back Costs	0.20	38.50	High value based on same chemical cost to "break" as "make" emulsion. Low value based on use of high speed centrifugal pump to break emulsion (no chemical).
d) Cargo Capacity Reduction (3% Volume)	1.59	1.20	High value based on 200,000 tanker at $0.40/barrel rate. Low values based on 20,000 tanker at $0.53/barrel rate.
Total	19.87	82.52	

II. Potential Cost Reductions - Through Cost Offsets

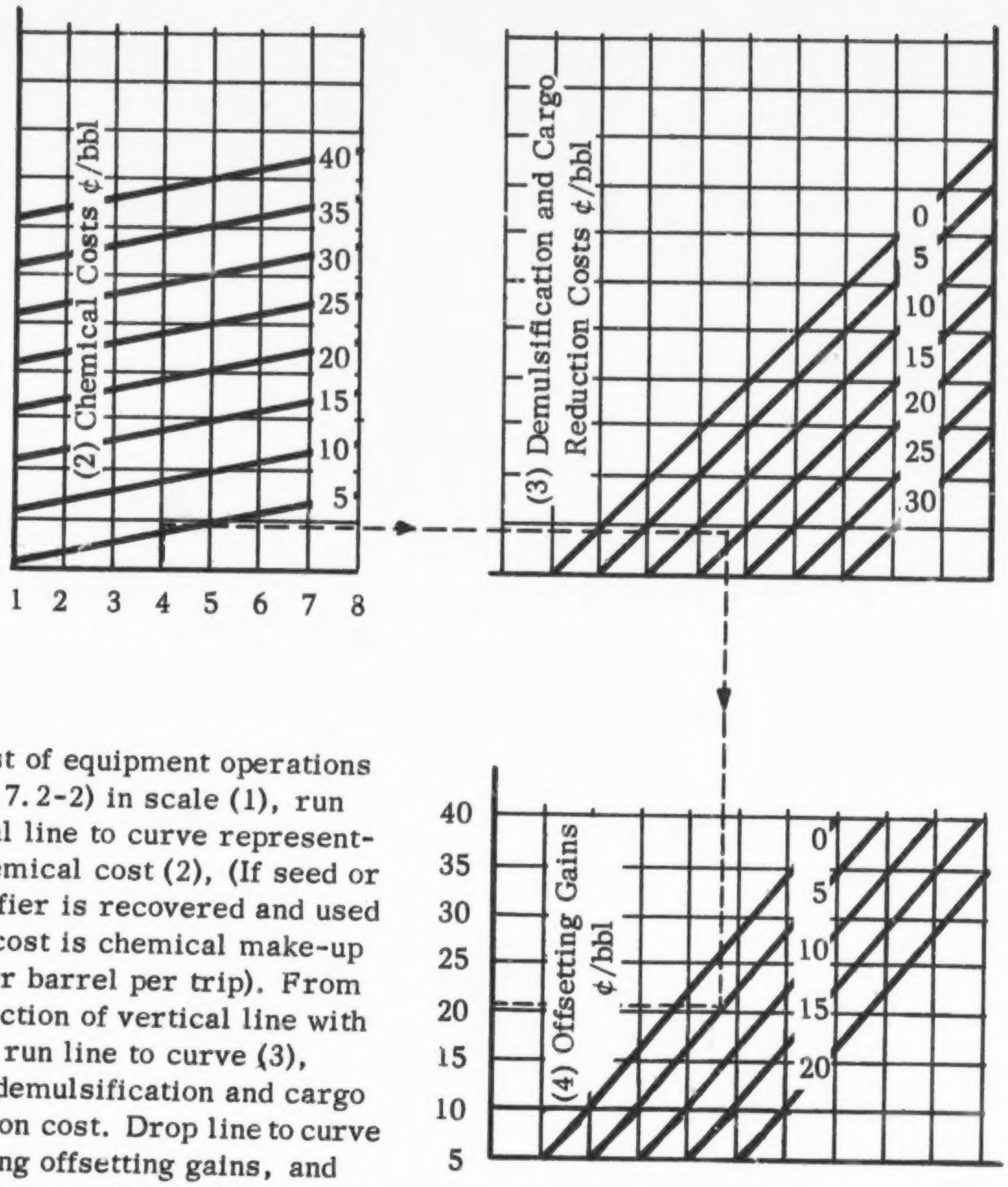
Item	Practical Range Low (¢/bbl.)	 High (¢/bbl.)	Notes of Explanation
a) Hazard Cost - Insurance and Clean Up	5.00	10.00	Low value based on estimate of loss per year of $300 million on transportation of 5.4 billion barrels (see Section 7.2.5 of this report). High value based on assumption that offsets from reduced ship hazards and frequency of ship accidents will increase with time, will double low value.
b) Crude Upgrading - Desalting	0.00	5.00	Reduction would range from none to 5 cents per barrel in those cases where reductions would eliminate any further desalting by the refinery.
c) Reduced Leakage and Cargo Evaporation	0.02	0.01	Estimated to equal cargo capacity reduction under I-d of this Table.
Total	5.02	15.01	

III. Potential Cost Reductions Through Procedure Modifications

Item	Practical Range Low (¢/bbl.)	 High (¢/bbl.)	Notes of Explanation
a) Return and Re-use Emulsion Seed Cargo Capacity Reduction 6.7%	3.6	2.7	Based on return of 6.7% of cargo as "emulsion seed" for re-use in next load. 30% loss of "emulsion seed" each trip.
b) Return and Re-use "External Phase" Cargo Capacity Reduction 2%	1.1	0.8	Based on returning 2/3 of aqueous phase for re-use, 1/3 must be discarded each trip to keep salinity from crude down.

FIGURE 7.2-1

OVERALL COST ESTIMATION



Put cost of equipment operations (Table 7.2-2) in scale (1), run vertical line to curve representing chemical cost (2), (If seed or emulsifier is recovered and used over, cost is chemical make-up cost per barrel per trip). From intersection of vertical line with curve, run line to curve (3), giving demulsification and cargo reduction cost. Drop line to curve (4) giving offsetting gains, and from intersection draw horizontal line to (5), "overall net cost of emulsification."

Dotted line represents 4¢/bbl operating and equipment cost to make emulsion, 6¢/bbl net chemical cost (27¢/bbl used 3 times), with 13¢ demulsification and cargo reduction charge, 5¢ benefit for desalting, insurance reduction, etc., giving an overall net cost of 21¢/bbl.

8. ACKNOWLEDGEMENTS

Many of the Sonics International, Inc. staff were asked for their advice or assistance during this study. Their support was invaluable and greatly appreciated.

Mr. M.G. Langhorne, Hunt Oil Company assisted in the procurement of foreign oils, and in providing handling and shipping information.

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Mr. R.G. Dulaney of Atlantic Pipe Line Company provided information on normal terminal operation.

Mr. Jack Frost of Ashland Chemical Company in Ashland, Kentucky, was kind enough to review the concept contemplated in this study, and give his thoughts and some of his employer's experience with their dispersant-Ridzlik.

Special thanks are due Mr. Glen White and his employer, Electro-Chem Laboratories, Inc. of Fort Worth, Texas, for their work to develop and supply the emulsifiers used in this study.

9. LIST OF PUBLICATIONS CRITICAL TO STUDY

Listed below are key references selected to provide a thorough understanding of the concept of handling crude oil and petroleum products in an emulsified state to reduce pollution and other hazards of an oil slick resulting from a catastrophe or negligence during the normal operation of tankers on the seas and waterways. Also included are key references to provide background knowledge of the problems and incidents which precipitated the search for methods to control oil pollution of the seas and waterways. For a more complete coverage of the literature, the reader is referred to the reference subsection of each section in the text of this report.

1. Battelle Memorial Institute, Pacific Northwest Laboratories, Oil Spillage Study; Literature Search and Critical to Control and Prevent Damage, November 20, 1967.

2. Benyon, L.R., The "Torrey Canyon" Incident, A review of Events, The British Petroleum Company, Ltd., September, 1967.

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10. GLOSSARY

1. API - American Petroleum Institute
2. ASTM - American Society of Testing Materials
3. bbl - barrel
4. bpm - barrels per minute
5. °C - degrees centigrade
6. continuous phase - the phase or liquid which forms the matrix in which the droplets (dispersed phase) are suspended
7. dispersed phase - the liquid which is present in the form of finely divided droplets
8. dwt - dead weight tons
9. displacement - state of being displaced
10. emulsion - a very fine dispersion of one liquid in another with which it is immiscible
11. °F - degrees Fahrenheit
12. gal - gallon, 3.78 liters
13. gpm - gallon per minute
14. hp - horsepower, 745 watts
15. in^3 - cubic inches
16. KHz - kilohertz
17. l - liter
18. ml - milliliter
19. mg/l - milligram per liter
20. ppm - parts per million
21. psi - pounds per square inch

22. % - percent

23. rpm - revolutions per minute

24. seed emulsion - dispersed phase distributed as colloidal particles in the continous phase by ultrasonic means

25. surfactant - surfacting agent, wetting agent

26. $TL_{50} = TL_m$ - median toxic limit to toxic materials

27. ton - 2,240 pounds (approximated as 7.5 barrels, 42 gallons each)

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5. Parker, T.J., "Approximate Hull Dimensions for 500,000 and 1,000,000 Deadweight Tankers", Shipping World and Shipbuilder, June, 1967.

6. The American Waterways Operators, Inc., 1967 Inland Waterborne Commerce Statistics, pp. 1, 2, 5, April, 1969.

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9. Battelle Memorial Institute, Oil Spillage Study; Literature Search and Critical Evaluation for Selection of Promising Techniques to Control and Prevent Damage, pp. 4-28 and 4-29, November 20, 1967.

10. "The Torrey Canyon", report presented to Parliament by the Secretary of State. London, England, Cmmd. 3246, April, 1967.

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SELECTION OF OILS AND PREPARATION AND TESTING OF EMULSIONS

Section 4.2

1. Patent applied for, Method for Forming Emulsions and Products Thereof.

Section 4.3

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Section 4.7

1. American Public Health Association, Inc., Standard Methods for the Examination of Water and Wastewater, Twelfth Edition, pp. 546-566, 1965.
2. "Oil Spillage Study and Literature Search and Critical Evaluation for Selection of Promising Techniques to Control and Prevent Damage", Pacific Northwest Laboratories of Battelle Memorial Institute, p. 6-8.
3. Loc cit, p 6-11
4. Loc cit, p 6-6
5. Loc cit, p 6-10
6. Loc cit, p 6-12 and 6-13
7. Loc cit, p 6-6 and 6-7, "Bunder Oil"
8. See Table 4.7-6, of this Report

Section 4.8

1. USAAV LABS Technical Report 67-62, 1967.

APPENDIX I

TABLE I-1

EVAPORATION RATE FROM LABORATORY DISH

CRUDE: ZUEITINA
EMULSIFIER: NONE
DEPTH OF FILL: HALF
VENTILATION: OPEN

DISH AREA, CM↑2 61
INITIAL SAMPLE WT, GMS: 30.5455

TIME IN		WT DISH +SAMPLE	CUMULATIVE WT LOSS			RATE OF WT LOSS	
MINUTES	DAYS	GRAMS	GRAMS	MG/CM↑2	LBS/FT↑2	MICRO-GMS /CM↑2 /SEC	LBS /FT↑2 /DAY
0	0	64.278	0				
1	0	64.18	.098	1.607	3>291E-3	26.78	4.739
2	0	64.099	.179	2.934.	6.011E-3	22.13	3.917
3	0	64.022	.256	4.197	8.597E-3	21.04	3.724
5	0	63.88	.398	6.525	1.337E-2	19.4	3.433
6	0	63.819	.459	7.525	1.541E-2	16.67	2.95
10	.01	63.599	.679	11.13	.0228	15.03	2.66
20	.01	63.193	1.085	17.79	3.644E-2	11.09	1.963
30	.02	62.898	1.38	22.62	4.634E-2	8.06	1.427
60	.04	62.241	2.037	33.39	6.841E-2	5.984	1.059
120	.08	61.318	2.96	48.53	.0994	4.203	.7439
240	.17	60.007	4.271	70.02	.1434	2.985	.5283
360	.25	59.095	5.183	84.97	.1741	2.077	.3675
500	.35	58.57	5.708	93.57	.1917	1.025	.1813
1470	1.02	57.283	6.995	114.7	.2349	.363	.0642

TABLE I-2

EVAPORATION RATE FROM LABORATORY DISH

CRUDE: ZUEITINA
EMULSIFIER: 1751
DEPTH OF FILL: HALF
VENTILATION: OPEN

DISH AREA, CM↑2 61
INITIAL SAMPLE WT, GMS: 27.2172

TIME IN		WT DISH +SAMPLE	CUMULATIVE WT LOSS			RATE OF WT LOSS	
MINUTES	DAYS	GRAMS	GRAMS	MG/CM↑2	LBS/FT↑2	MICRO-GMS /CM↑2 /SEC	LBS /FT↑2 /DAY
0	0	64.2642	0				
1	0	64.242	.0222	.364	7.455E-4	6.066	1.074
2	0	64.225	.0392	.643	1.316E-3	4.645	.8221
3	0	64.213	.0512	.839	1.719E-3	3.279	.5803
5	0	64.18	.0842	1.38	2.826E-3	4.508	.7979
6	0	64.17	.0942	1.544	3.163E-3	2.732	.4836
10	.01	64.136	.1282	2.102	4.305E-3	2.322	.411
20	.01	64.09	.1742	2.856	5.85E-3	1.257	.2224
30	.02	64.07	.1942	3.184	6.522E-3	.546	.0967
60	.04	64.0038	.2604	4.269	8.745E-3	.603	.1067
120	.08	63.9256	.3386	5.551	1.137E-2	.356	.063
226	.16	63.8141	.4501	7.379	1.512E-2	.287	.0509
411	.29	63.6817	.5825	9.549	1.956E-2	.196	.0346
567	.39	63.6021	.6621	10.85	2.223E-2	.139	.0247
1110	.77	63.3134	.9508	15.59	3.193E-2	.145	.0257

TABLE I-3

EVAPORATION RATE FROM LABORATORY DISH

CRUDE: ZUEITINA
EMULSIFIER: 1752
DEPTH OF FILL: HALF
VENTILATION: OPEN

DISH AREA, CM↑2 61
INITIAL SAMPLE WT, GMS: 25.2705

TIME IN		WT DISH +SAMPLE	CUMULATIVE WT LOSS			RATE OF WT LOSS	
MINUTES	DAYS	GRAMS	GRAMS	MG/CM↑2	LBS/FT↑2	MICRO-GMS /CM↑2 /SEC	LBS /FT↑2 /DAY
0	0	58.966	0				
1	0	58.95	.016	.262	5.373E-4	4.372	.7737
2	0	58.934	.032	.525	1.075E-3	4.372	.7737
3	0	58.921	.045	.738	1.511E-3	3.552	.6286
5	0	58.892	.074	1.213	2.485E-3	3.962	.7012
6	0	58.878	.088	1.443	2.955E-3	3.825	.677
10	.01	58.841	.125	2.049	4.198E-3	2.527	.4473
20	.01	58.787	.179	2.934	6.011E-3	1.475	.2611
30	.02	58.755	.211	3.459	7.086E-3	.874	.1547
60	.04	58.7178	.2482	4.069	8.335E-3	.339	.06
126	.09	58.6811	.2849	4.67	9.567E-3	.152	.0269
240	.17	58.6383	.3277	5.372	.011	.103	.0182
386	.27	58.524	.442	7.246	1.484E-2	.214	.0379
702	.49	58.361	.605	9.918	2.032E-2	.141	.0249

TABLE I-4

EVAPORATION RATE FROM LABORATORY DISH

CRUDE: ZUEITINA
EMULSIFIER: 1752
DEPTH OF FILL: HALF
VENTILATION: OPEN

DISH AREA, CM↑2 61
INITIAL SAMPLE WT, GMS: 27.122

TIME IN		WT DISH +SAMPLE	CUMULATIVE WT LOSS			RATE OF WT LOSS	
MINUTES	DAYS	GRAMS	GRAMS	MG/CM↑2	LBS/FT↑2	MICRO-GMS /CM↑2 /SEC	LBS /FT↑2 /DAY
0	0	68.395	0				
1	0	68.383	.012	.197	4.03E-4	3.279	.5803
2	0	68.365	.03	.492	1.007E-3	4.918	.8704
3	0	68.352	.043	.705	1.444E-3	3.552	.6286
5	0	58.335	10.06	164.9	.3378	1368.	242.2
7	0	68.318	.077	1.262	2.586E-3	-1364.	-241.4
10	.01	68.299	.096	1.574	3.224E-3	1.73	.3063
20	.01	68.23	.165	2.705	5.541E-3	1.885	.3337
30	.02	68.171	.224	3.672	7.522E-3	1.612	.2853
60	.04	68.035	.36	5.902	1.209E-2	1.239	.2192
104	.07	67.889	.506	8.295	1.699E-2	.907	.1605
1560	1.08	66.208	2.187	35.85	7.344E-2	.315	.0558

TABLE I-5

EVAPORATION RATE FROM LABORATORY DISH

CRUDE: TIA JUANA
EMULSIFIER: NONE
DEPTH OF FILL: HALF
VENTILATION: OPEN

DISH AREA, CM↑2 61
INITIAL SAMPLE WT, GMS: 42.7578

TIME	IN	WT DISH +SAMPLE	CUMULATIVE WT LOSS			RATE OF WT LOSS	
MINUTES	DAYS	GRAMS	GRAMS	MG/CM↑2	LBS/FT↑2	MICRO-GMS /CM↑2 /SEC	LBS /FT↑2 /DAY
0	0	81.89	0				
1	0	81.86	.03	.492	1.007E-3	8.197	1.451
2	0	81.832	.058	.951	1.948E-3	7.65	1.354
3	0	81.808	.082	1.344	2.754E-3	6.557	1.161
5	0	81.755	.135	2.213	4.534E-3	7.24	1.282
6	0	81.728	.162	2.656	5.44E-3	7.377	1.306
10	.01	81.62	.27	4.426	9.067E-3	7.377	1.306
20	.01	81.482	.408	6.689	.0137	3.77	.6673
30	.02	81.359	.531	8.705	1.783E-2	3.361	.5948
60	.04	81.0195	.8705	14.27	2.923E-2	3.092	.5472
120	.08	80.55	1.34	21.97	.045	2.138	.3784
273	.19	79.962	1.928	31.61	6.475E-2	1.05	.1858
335	.23	79.763	2.127	34.87	7.143E-2	.877	.1552
1320	.92	78.1321	3.7579	61.61	.1262	.452	.0801
4320	3	76.7459	5.1441	84.33	.1727	.126	.0223
15840	11	75.298	6.592	108.1	.2214	.034	.0061
36000	25	74.418	7.472	122.5	.2509	.012	.0021

TABLE I-6

EVAPORATION RATE FROM LABORATORY DISH

CRUDE: TIA JUANA
EMULSIFIER: 1751
DEPTH OF FILL: HALF
VENTILATION: OPEN

DISH AREA, CM↑2 61
INITIAL SAMPLE WT, GMS: 26.2585

T I M E MINUTES	I N DAYS	WT DISH +SAMPLE GRAMS	CUMULATIVE WT LOSS GRAMS	MG/CM↑2	LBS/FT↑2	RATE OF WT LOSS MICRO-GMS /CM↑2 /SEC	LBS /FT↑2 /DAY
0	0	61.705	0				
1	0	61.696	.009	.148	3.022E-4	2.459	.4352
2	0	61.691	.014	.23	4.701E-4	1.366	.2418
3	0	60.686	1.019	16.71	3.422E-2	274.6	48.6
5	0	61.6755	.0295	.484	9.907E-4	-135.2	-23.92
7	0	61.6655	.0395	.648	1.326E-3	1.366	.2418
10	.01	61.652	.053	.869	1.78E-3	1.23	.2176
20	.01	61.6156	.0894	1.466	3.002E-3	.995	.176
30	.02	61.584	.121	1.984	4.063E-3	.863	.1528
60	.04	61.505	.2	3.279	6.716E-3	.719	.1273
120	.08	61.383	.322	5.279	1.081E-2	.556	.0983
240	.17	61.19	.515	8.443	1.729E-2	.439	.0778
1000	.69	60.42	1.285	21.07	4.315E-2	.277	.049
2000	1.39	60.078	1.627	26.67	5.464E-2	.093	.0165
3960	2.75	59.37	2.335	38.28	7.841E-2	.099	.0175
9840	6.83	58.492	3.213	52.67	.1079	.041	.0072
15960	11.08	57.673	4.032	66.1	.1354	.037	.0065
34260	23.79	56.5278	5.1772	84.87	.1739	.017	.003

TABLE I-7

EVAPORATION RATE FROM LABORATORY DISH

CRUDE: TIA JUANA
EMULSIFIER: 1752
DEPTH OF FILL: HALF
VENTILATION: OPEN

DISH AREA, CM↑2 61
INITIAL SAMPLE WT, GMS: 32.0191

TIME IN		WT DISH +SAMPLE	CUMULATIVE WT LOSS			RATE OF WT LOSS	
MINUTES	DAYS	GRAMS	GRAMS	MG/CM↑2	LBS/FT↑2	MICRO-GMS /CM↑2 /SEC	LBS /FT↑2 /DAY
0	0	67.127	0				
1	0	67.119	.008	.131	2.687E-4	2.186	.3869
2	0	67.112	.015	.246	5.037E-4	1.913	.3385
3	0	67.106	.021	.344	7.052E-4	1.639	.2901
5	0	67.094	.033	.541	1.108E-3	1.639	.2901
7	0	67.0835	.0435	.713	1.461E-3	1.434	.2539
10	.01	67.069	.058	.951	1.948E-3	1.321	.2337
20	.01	67.035	.092	1.508	3.09E-3	.929	.1644
30	.02	66.997	.13	2.131	4.366E-3	1.038	.1838
60	.04	66.96	.167	2.738	5.608E-3	.337	.0596
120	.08	66.763	.364	5.967	1.222E-2	.897	.1588
900	.63	65.887	1.24	20.33	4.164E-2	.307	.0543
4140	2.88	64.511	2.616	42.89	8.785E-2	.116	.0205
8220	5.71	63.634	3.493	57.26	.1173	.059	.0104
15960	11.08	61.855	5.272	86.43	.177	.063	.0111
37020	25.71	60.634	6.493	106.4	.218	.016	.0028

TABLE I-8

EVAPORATION RATE FROM LABORATORY DISH

CRUDE: NO.6 FUEL OIL
EMULSIFIER: NONE
DEPTH OF FILL: HALF
VENTILATION: OPEN

DISH AREA, CM↑2 61
INITIAL SAMPLE WT, GMS: 37.408

TIME IN MINUTES	DAYS	WT DISH +SAMPLE GRAMS	CUMULATIVE WT LOSS GRAMS	MG/CM↑2	LBS/FT↑2	RATE OF WT LOSS MICRO-GMS /CM↑2 /SEC	LBS /FT↑2 /DAY
0	0	68.538	0				
1	0	68.538	0	0	0	0	0
2	0	68.538	0	0	0	0	0
3	0	68.538	0	0	0	0	0
5	0	68.5375	.0005	.008	1.679E-5	.068	.0121
7	0	68.537	.001	.016	3.358E-5	.068	.0121
10	.01	68.5365	.0015	.025	5.037E-5	.046	.0081
20	.01	68.5363	.0017	.028	5.709E-5	.005	.001
30	.02	68.5358	.0022	.036	7.388E-5	.014	.0024
60	.04	68.5323	.0057	.093	1.914E-4	.032	.0056
120	.08	68.5258	.0122	.2	4.097E-4	.03	.0052
1560	1.08	68.4492	.0888	1.456	2.982E-3	.015	.0026
4080	2.83	68.342	.196	3.213	6.582E-3	.012	.0021
10080	7	68.191	.347	5.689	1.165E-2	.007	.0012
16000	11.11	67.923	.615	10.08	2.065E-2	.012	.0022

TABLE I-9

EVAPORATION RATE FROM LABORATORY DISH

CRUDE: NO.6 FUEL OIL
EMULSIFIER: 1751
DEPTH OF FILL: HALF
VENTILATION: OPEN

DISH AREA, CM↑2 61
INITIAL SAMPLE WT, GMS: 37.8312

TIME IN MINUTES	DAYS	WT DISH +SAMPLE GRAMS	CUMULATIVE WT LOSS GRAMS	MG/CM↑2	LBS/FT↑2	RATE OF WT LOSS MICRO-GMS /CM↑2 /SEC	LBS /FT↑2 /DAY
0	0	71.745	0				
1	0	71.743	.002	.033	6.716E-5	.546	.0967
2	0	71.742	.003	.049	1.007E-4	.273	.0484
3	0	71.741	.004	.066	1.343E-4	.273	.0484
5	0	71.7395	.0055	.09	1.847E-4	.205	.0363
7	0	71.736	.009	.148	3.022E-4	.478	.0846
10	.01	71.7315	.0135	.221	4.534E-4	.41	.0725
20	.01	71.717	.028	.459	9.403E-4	.396	.0701
30	.02	71.704	.041	.672	1.377E-3	.355	.0629
60	.04	71.6725	.0725	1.189	2.435E-3	.287	.0508
120	.08	71.625	.12	1.967	4.03E-3	.216	.0383
240	.17	71.562	.183	3.	6.145E-3	.143	.0254
390	.27	71.497	.248	4.066	8.328E-3	.118	.021
1440	1	71.338	.407	6.672	1.367E-2	.041	.0073
3120	2.17	71.161	.584	9.574	1.961E-2	.029	.0051
7200	5	70.89	.855	14.02	2.871E-2	.018	.0032
15960	11.08	70.594	1.151	18.87	3.865E-2	.009	.0016
36030	25>02	70.2906	1.4544	23.84	4.884E-2	.004	.0007

TABLE I-10

EVAPORATION RATE FROM LABORATORY DISH

CRUDE: NO.6 FUEL OIL
EMULSIFIER: 1752
DEPTH OF FILL: HALF
VENTILATION: OPEN

DISH AREA, CM↑2 61
INITIAL SAMPLE WT, GMS: 42.7542

T I M E	I N	WT DISH +SAMPLE	CUMULATIVE WT LOSS			RATE OF WT LOSS	
						MICRO-GMS	LBS
MINUTES	DAYS	GRAMS	GRAMS	MG/CM↑2	LBS/FT↑2	/CM↑2 /SEC	/FT↑2 /DAY
0	0	71.572	0				
1	0	71.57	.002	.033	6.716E-5	.546	.0967
2	0	71.569	.003	.049	1.007E-4	.273	.0484
3	0	71.567	.005	.082	1.679E-4	.546	.0967
5	0	71.563	.009	.148	3.022E-4	.546	.0967
7	0	71.56	.012	.197	4.03E-4	.41	.0725
10	.01	71.555	.017	.279	5.709E-4	.455	.0806
20	.01	71.541	.031	.508	1.041E-3	.383	.0677
30	.02	71.524	.048	.787	1.612E-3	.464	.0822
60	.04	71.497	.075	1.23	2.519E-3	.246	.0435
120	.08	71.457	.115	1.885	3.862E-3	.182	.0322
240	.17	71.397	.175	2.869	5>877E-3	.137	.0242
360	.25	71.37	.202	3.311	6.783E-3	.061	.0109
1400	.97	71.165	.407	6.672	1.367E-2	.054	.0095
2880	2	71.07	.502	8.23	1.686E-2	.018	.0031
17280	12	70.51	1.062	17.41	3.566E-2	.011	.0019

TABLE I-11

EVAPORATION RATE FROM LABORATORY DISH

CRUDE: ZUEITINA
EMULSIFIER: NONE
DEPTH OF FILL: HALF
VENTILATION: 1/4 INCH VENT

DISH AREA, CM↑2 61
INITIAL SAMPLE WT, GMS: 31.7295

TIME IN MINUTES	DAYS	WT DISH +SAMPLE GRAMS	CUMULATIVE WT LOSS GRAMS	MG/CM↑2	LBS/FT↑2	RATE OF WT LOSS MICRO-GMS /CM↑2 /SEC	LBS /FT↑2 /DAY
0	0	97.169	0				
1	0	97.164	.005	.082	1.679E-4	1.366	.2418
2	0	97.1603	.0087	.143	2.922E-4	1.011	.1789
3	0	97.156	.013	.213	4.366E-4	1.175	.2079
5	0	97.1494	.0196	.321	6.582E-4	.902	.1596
7	0	97.143	.026	.426	8.731E-4	.874	.1547
10	.01	97.132	.037	.607	1.243E-3	1.002	.1773
20	.01	97.105	.064	1.049	2.149E-3	.738	.1306
30	.02	97.068	.101	1.656	3.392E-3	1.011	.1789
60	.04	96.996	.173	2.836	5.81E-3	.656	.1161
120	.08	96.836	.333	5.459	1.118E-2	.729	.129
240	.17	96.546	.623	10.21	2.092E-2	.66	.1169
360	.25	96.415	.754	12.36	2.532E-2	.298	.0528
780	.54	96.0297	1.1393	18.68	3.826E-2	.251	.0444
1470	1.02	95.57	1.599	26.21	.0537	.182	.0322
4320	3	94.475	2.694	44.16	9.047E-2	.105	.0186
8640	6	93.4466	3.7224	61.02	.125	.065	.0115
16000	11.11	92.216	4.953	81.2	.1663	.046	.0081

TABLE I-12

EVAPORATION RATE FROM LABORATORY DISH

CRUDE: ZUEITINA
EMULSIFIER: 1751
DEPTH OF FILL: HALF
VENTILATION: 1/4 INCH VENT

DISH AREA, CM↑2 61
INITIAL SAMPLE WT, GMS: 24.6865

TIME IN		WT DISH +SAMPLE	CUMULATIVE WT LOSS			RATE OF WT LOSS	
MINUTES	DAYS	GRAMS	GRAMS	MG/CM↑2	LBS/FT↑2	MICRO-GMS /CM↑2 /SEC	LBS /FT↑2 /DAY
0	0	94.879	0				
1	0	94.876	.003	.049	1.007E-4	.82	.1451
2	0	94.874	.005	.082	1.679E-4	.546	.0967
3	0	94.871	.008	.131	2.687E-4	.82	.1451
5	0	94.866	.013	.213	4.366E-4	.683	.1209
7	0	94.861	.018	.295	6.045E-4	.683	.1209
10	.01	94.854	.025	.41	8.395E-4	.638	.1128
20	.01	94.832	.047	.77	1.578E-3	.601	.1064
30	.02	94.807	.072	1.18	2.418E-3	.683	.1209
60	.04	94.75	.129	2.115	4.332E-3	.519	.0919
120	.08	94.652	.227	3.721	7.623E-3	.446	.079
240	.17	94.495	.384	6.295	.0129	.357	.0633
600	.42	94.2079	.6711	11.	2.254E-2	.218	.0386
1140	.79	92.903	1.976	32.39	6.636E-2	.66	.1169
2520	1.75	92.858	2.021	33.13	6.787E-2	.009	.0016
5460	3.79	91.823	3.056	50.1	.1026	.096	.017
10080	7	90.6286	4.2504	69.68	.1427	.071	.0125
16000	11.11	89.4978	5.3812	88.22	.1807	.052	.0092

TABLE I-13

EVAPORATION RATE FROM LABORATORY DISH

CRUDE: ZUEITINA
EMULSIFIER: 1752
DEPTH OF FILL: HALF
VENTILATION: 1/4 INCH VENT

DISH AREA, CM↑2 61
INITIAL SAMPLE WT, GMS: 26.325

TIME IN		WT DISH +SAMPLE	CUMULATIVE WT LOSS			RATE OF WT LOSS	
MINUTES	DAYS	GRAMS	GRAMS	MG/CM↑2	LBS/FT↑2	MICRO-GMS /CM↑2 /SEC	LBS /FT↑2 /DAY
0	0	95,797	0				
1	0	95.792	.005	.082	1.679E-4	1.366	.2418
2	0	95.789	.008	.131	2.687E-4	.82	.1451
3	0	95.785	.012	.197	4.03E-4	1.093	.1934
5	0	95.?78	.019	>311	6>38E-4	.956	.1693
7	0	95.W75	.022	.361	7.388E-4	.41	.0725
13	.01	95.755	.042	.689	1.41E-3	.911	.1612
20	.01	95.735	.062	1.016	2.082E-3	.781	.1382
30	.02	95.705	.092	1.508	3.09E-3	.82	.1451
60	.04	95.644	.153	2.508	5.138E-3	.556	.0983
120	.08	95.527	.27	4.426	9.067E-3	.533	.0943
600	.42	95.085	.712	11.67	2.391E-2	.252	.0445
1080	.75	94.525	1.272	20.85	4.272E-2	.319	.0564
1860	1.29	93.885	1.912	31.34	6.421E-2	.224	.0397
5520	3.83	92.709	3.088	50.62	.1037	.088	.0155
10080	7	91.551	4.246	69.61	.1426	.069	.0123
16000	11.11	90.0688	5.7282	93.9	.1924	.068	.0121

TABLE I-14

EVAPORATION RATE FROM LABORATORY DISH

CRUDE: TIA JUANA
EMULSIFIER: NONE
DEPTH OF FILL: HALF
VENTILATION: 1/4 INCH VENT

DISH AREA, CM↑2 61
INITIAL SAMPLE WT, CMS: 19.9708

TIME	IN	WT DISH	CUMULATIVE WT LOSS			RATE OF WT LOSS	
		+SAMPLE				MICRO-GMS	LBS
MINUTES	DAYS	GRAMS	GRAMS	MG/CM↑2	LBS/FT↑2	/CM↑2 /SEC	/FT↑2 /DAY
0	0	92.418	0				
1	0	92.415	.003	.049	1.007E-4	.82	.1451
2	0	92.413	.005	.082	1.679E-4	.546	.0967
3	0	92.4105	.0075	.123	2.519E-4	.683	.1209
5	0	92.406	.012	.197	4.03E-4	.615	.1088
7	0	92.402	.016	.262	5.373E-4	.546	.0967
10	.01	92.394	.024	.393	8.06E-4	.729	.129
20	.01	92.3753	.0427	.7	1.434E-3	.511	.0904
30	.02	92.358	.06	.984	2.015E-3	.473	.0837
60	.04	92.313	.105	1.721	3.526E-3	.41	.0725
120	.08	92.237	.181	2.967	6.078E-3	.346	.0613
240	.17	92.126	.292	4.787	9.806E-3	.253	.0447
1000	.69	91.755	.663	10.87	2.226E-2	.133	.0236
2640	1.83	91.436	.982	16.1	3.298E-2	.053	.0094
6960	4.83	90.993	1.425	23.36	4.785E-2	.028	.005
16000	11.11	90.6652	1.7528	28.73	5.886E-2	.01	.0018

TABLE I-15

EVAPØRATIØN RATE FRØM LABØRATØRY DISH

CRUDE: TIA JUANA
EMULSIFIER: 1751
DEPTH ØF FILL: HALF
VENTILATIØN: 1/4 INCH VENT

DISH AREA, CM↑2 61
INITIAL SAMPLE WT, GMS: 29.511

TIME IN		WT DISH +SAMPLE	CUMULATIVE WT LØSS			RATE ØF WT LØSS	
MINUTES	DAYS	GRAMS	GRAMS	MG/CM↑2	LBS/FT↑2	MICRØ-GMS /CM↑2 /SEC	LBS /FT↑2 /DAY
0	0	94.744	0				
1	0	94.74	.004	.066	1.343E-4	1.093	.1934
2	0	94.736	.008	.131	2.687E-4	1.093	.1934
3	0	94.732	.012	.197	4.03E-4	1.093	.1934
5	0	94.731	.013	.213	4.366E-4	.137	.0242
7	0	94.729	.015	.246	5.037E-4	.273	.0484
10	.01	94.725	.019	.311	6.38E-4	.364	.0645
20	.01	94.714	.03	.492	1.007E-3	.301	.0532
30	.02	94.701	.043	.705	1.444E-3	.355	.0629
60	.04	94.675	.069	1.131	2.317E-3	.237	.0419
120	.08	94.622	.122	2.	4.097E-3	.241	.0427
240	.17	94.515	.229	3.754	7.69E-3	.244	.0431
400	.28	94.46	.284	4.656	9.537E-3	.094	.0166
742	.52	94.23	.514	8.426	1.726E-2	.184	.0325
1440	1	93.95	.794	13.02	2.666E-2	.11	.0194
4320	3	93.203	1.541	25.26	5.175E-2	.071	.0125
8640	6	92.621	2.123	34.8	7.129E-2	.037	.0065
16000	11.11	91.9507	2.7933	45.79	.0938	.025	.0044

TABLE I-16

EVAPORATION RATE FROM LABORATORY DISH

CRUDE: TIA JUANA
EMULSIFIER: 1752
DEPTH OF FILL: HALF
VENTILATION: 1/4 INCH VENT

DISH AREA, CM↑2 61
INITIAL SAMPLE WT, CMS: 29.402

T I M E	I N	WT DISH +SAMPLE	CUMULATIVE WT LOSS			RATE OF WT LOSS	
MINUTES	DAYS	GRAMS	GRAMS	MG/CM↑2	LBS7FT↑2	MICRO-GMS /CM↑2 ·/SEC	LBS /FT↑2 /DAY
0	0	101.491	0				
1	0	101.48	.011	.18	3.694E-4	3.005	.5319
2	0	101.475	.016	.262	5.373E-4	1.366	.2418
3	0	101.473	.018	.295	6.045E-4	.546	.0967
5	0	101.471	.02	.328	6.716E-4	.273	.0484
7	0	101.467	.024	.393	8.06E-4	.546	.0967
10	.01	101.464	.027	.443	9.067E-4	.273	.0484
20	.01	101.455	.036	.59	1.209E-3	.246	.0435
30	.02	101.436	.055	.902	1.847E-3	.519	.0919
60	.04	101.416	.075	1.23	2.519E-3	.182	.0322
120	.08	101.355	.136	2.23	4.567E-3	.278	.0492
240	.17	101.3	.191	3.131	6.414E-3	.125	.0222
796	.55	101.109	.382	6.262	1.283E-2	.094	.0166
1140	.79	100.781	.71	11.64	2.384E-2	.261	.0461
4020	2.79	99.984	1.507	24.71	5.061E-2	.076	.0134
8640	6	99.391	2.1	34.43	7.052E-2	.035	.0062
16000	11.11	98.952	2.539	41.62	8.526E-2	.016	.0029

TABLE I-17

EVAPORATION RATE FROM LABORATORY DISH

CRUDE: NO.6 FUEL OIL
EMULSIFIER: NONE
DEPTH OF FILL: HALF
VENTILATION: 1/4 INCH VENT

DISH AREA, CM↑2 61
INITIAL SAMPLE WT, GMS: 35.7328

TIME IN MINUTES	TIME IN DAYS	WT DISH +SAMPLE GRAMS	CUMULATIVE WT LOSS GRAMS	CUMULATIVE WT LOSS MG/CM↑2	CUMULATIVE WT LOSS LBS/FT↑2	RATE OF WT LOSS MICRO-GMS /CM↑2 /SEC	RATE OF WT LOSS LBS /FT↑2 /DAY
0	0	103.955	0				
1	0	103.955	0	0	0	0	0
2	0	103.954	.001	.016	3.358E-5	.273	.0484
3	0	103.953	.002	.033	6.716E-5	.273	.0484
5	0	103.953	.002	.033	6.716E-5	0	0
7	0	103.952	.003	.049	1.007E-4	.137	.0242
10	.01	103.952	.003	.049	1.007E-4	0	0
20	.01	103.951	.004	.066	1.343E-4	.027	.0048
30	.02	103.95	.005	.082	1.679E-4	.027	.0048
60	.04	103.948	.007	.115	2.351E-4	.018	.0032
120	.08	103.943	.012	.197	4.03E-4	.023	.004
360	.25	103.935	.02	.328	6.716E-4	.009	.0016
1380	.96	103.916	.039	.639	1.31E-3	.005	.0009
5760	4	103.853	.102	1.672	3.425E-3	.004	.0007
16000	11.11	103.796	.159	2.607	5.339E-3	.002	.0003

TABLE I-18

EVAPORATION RATE FROM LABORATORY DISH

CRUDE: NO.6 FUEL OIL
EMULSIFIER: 1751
DEPTH OF FILL: HALF
VENTILATION: 1/4 INCH VENT

DISH AREA, CM↑2 61
INITIAL SAMPLE WT, GMS: 30.3945

TIME IN		WT DISH +SAMPLE	CUMULATIVE WT LOSS			RATE OF WT LOSS	
MINUTES	DAYS	GRAMS	GRAMS	MG/CM↑2	LBS/FT↑2	MICRO-GMS /CM↑2 /SEC	LBS /FT↑2 /DAY
0	0	97.241	0				
1	0	97.241	0	0	0	0	0
2	0	97.2408	.0002	.003	6.716E-6	.055	.0097
3	0	97.2406	.0004	.007	1.343E-5	.055	.0097
5	0	97.24	.001	.016	3.358E-5	.082	.0145
7	0	97.2395	.0015	.025	5.037E-5	.068	.0121
10	.01	97.2385	.0025	.041	8.395E-5	.091	.0161
20	.01	97.235	.006	.098	2.015E-4	.096	.0169
30	.02	97.232	.009	.148	3.022E-4	.082	.0145
60	.04	97.2239	.0171	.28	5.742E-4	.074	.0131
120	.08	97.215	.026	.426	8.731E-4	.041	.0072
240	.17	97.205	.036	.59	1.209E-3	.023	.004
360	.25	97.1915	.0495	.811	1.662E-3	.031	.0054
1440	1	97.162	.079	1.295	2.653E-3	.007	.0013
5760	4	97.033	.208	3.41	6.985E-3	.008	.0014
16000	11.11	96.8452	.3958	6.489	1.329E-2	.005	.0009

TABLE I-19

EVAPORATION RATE FROM LABORATORY DISH

CRUDE: NO.6 FUEL OIL
EMULSIFIER: 1752
DEPTH OF FILL: HALF
VENTILATION: 1/4 INCH VENT

DISH AREA, CM↑2 61
INITIAL SAMPLE WT, GMS: 43.752

TIME IN MINUTES	IN DAYS	WT DISH +SAMPLE GRAMS	CUMULATIVE WT LOSS GRAMS	CUMULATIVE WT LOSS MG/CM↑2	CUMULATIVE WT LOSS LBS/FT↑2	RATE OF WT LOSS MICRO-GMS /CM↑2 /SEC	RATE OF WT LOSS LBS /FT↑2 /DAY
0	0	110.297	0				
1	0	110.296	.001	.016	3.358E-5	.273	.0484
2	0	110.296	.001	.016	3.358E-5	0	0
3	0	110.295	.002	.033	6.716E-5	.273	.0484
5	0	110.295	.002	.033	6.716E-5	0	0
7	0	110.294	.003	.049	1.007E-4	.137	.0242
10	.01	110.293	.004	.066	1.343E-4	.091	.0161
20	.01	110.29	.007	.115	2.351E-4	.082	.0145
30	.02	110.286	.011	.18	3.694E-4	.109	.0193
60	.04	110.28	.017	.279	5.709E-4	.055	.0097
120	.08	110.265	.032	.525	1.075E-3	.068	.0121
240	.17	110.245	.052	.852	1.746E-3	.046	.0081
480	.33	110.206	.091	1.492	3.056E-3	.044	.0079
1440	1	110.113	.184	3.016	6.179E-3	.026	.0047
5760	4	109.87	.427	7.	1.434E-2	.015	.0027
11460	7.96	109.765	.532	8.721	1.787E-2	.005	.0009

TABLE I-20

EVAPORATION RATE FROM LABORATORY DISH

CRUDE: ZUEITINA
EMULSIFIER: NONE
DEPTH OF FILL: FULL
VENTILATION: OPEN

DISH AREA, CM↑2 61
INITIAL SAMPLE WT, CMS: 77.649

TIME IN		WT DISH +SAMPLE	CUMULATIVE WT LOSS			RATE OF WT LOSS	
MINUTES	DAYS	GRAMS	GRAMS	MG/CM↑2	LBS/FT↑2	MICRO-GMS /CM↑2 /SEC	LBS /FT↑2 /DAY
0	0	113.413	0				
1	0	113.21	.203	3.328	6.817E-3	55.46	9.817
2	0	113.04	.373	6.115	1.253E-2	46.45	8.221
3	0	112.882	.531	8.705	1.783E-2	43.17	7.641
5	0	112.585	.828	13.57	2.781E-2	40.57	7.181
6	0	112.301	1.112	18.23	3.734E-2	77.6	13.73
10	.01	111.99	1.423	23.33	4.779E-2	21.24	3.76
20	.01	111.2	2.213	36.28	7.432E-2	21.59	3.82
30	.02	110.625	2.788	45.71	9.363E-2	15.71	2.781
60	.04	109.329	4.084	66.95	.1371	11.8	2.089
120	.08	107.02	6.393	104.8	.2147	10.52	1.861
180	.13	106.53	6.883	112.8	.2311	2.231	.3949

TABLE I-21

EVAPORATION RATE FROM LABORATORY DISH

CRUDE: ZUEITINA
EMULSIFIER: 1751
DEPTH OF FILL: FULL
VENTILATION: OPEN

DISH AREA, CM↑2 61
INITIAL SAMPLE WT, GMS: 70.3912

TIME IN MINUTES	DAYS	WT DISH +SAMPLE GRAMS	CUMULATIVE WT LOSS GRAMS	MG/CM↑2	LBS/FT↑2	RATE OF WT LOSS MICRO-GMS /CM↑2 /SEC	LBS /FT↑2 /DAY
0	0	106.675	0				
1	0	106.657	.018	.295	6.045E-4	4.918	.8704
2	0	106.633	.042	.689	1.41E-3	6.557	1.161
3	0	106.62	.055	.902	1.847E-3	3.552	.6286
5	0	106.6	.075	1.23	2.519E-3	2.732	.4836
6	0	106.591	.084	1.377	2.821E-3	2.459	.4352
10	.01	106.567	.108	1.77	3.627E-3	1.639	.2901
20	.01	106.532	.143	2.344	4.802E-3	.956	.1693
30	.02	106.51	.165	2.705	5.541E-3	.601	.1064
60	.04	106.471	.204	3.344	6.851E-3	.355	.0629
120	.08	106.415	.26	4.262	8.731E-3	.255	.0451
240	.17	106.265	.41	6.721	1.377E-2	.342	.0604
490	.34	106.204	.471	7.721	1.582E-2	.067	.0118
1065	.74	105.977	.698	11.44	2.344E-2	.108	.0191
1820	1.26	105.271	1.404	23.02	4.715E-2	.255	.0452
2950	2.05	104.586	2.089	34.25	7.015E-2	.166	.0293
6130	4.26	102.386	4.289	70.31	.144	.189	.0335
14220	9.88	100.515	6.16	101.	.2069	.063	.0112
36000	25	95.629	11.046	181.1	.3709	.061	.0108

TABLE I-22

EVAPORATION RATE FROM LABORATORY DISH

CRUDE: ZUEITINA
EMULSIFIER: 1752
DEPTH OF FILL: FULL
VENTILATION: OPEN

DISH AREA, CM↑2 61
INITIAL SAMPLE WT, CMS: 76.6614

TIME IN		WT DISH +SAMPLE	CUMULATIVE WT LOSS			RATE OF WT LOSS	
MINUTES	DAYS	GRAMS	GRAMS	MG/CM↑2	LBS/FT↑2	MICRO-GMS /CM↑2 /SEC	LBS /FT↑2 /DAY
0	0	112.385	0				
1	0	112.365	.02	.328	6.716E-4	5.464	.9671
2	0	112.348	.037	.607	1.243E-3	4.645	.8221
3	0	112.331	.054	.885	1.813E-3	4.645	.8221
5	0	112.304	.081	1.328	2.72E-3	3.689	.6528
6	0	112.294	.091	1.492	3.056E-3	2.732	.4836
10	.01	112.265	.12	1.967	4.03E-3	1.981	.3506
20	.01	112.215	.17	2.787	5.709E-3	1.366	.2418
30	.02	112.185	.2	3.279	6.716E-3	.82	.1451
60	.04	112.15	.235	3.852	7.892E-3	.319	.0564
120	.08	112.121	.264	4.328	8.866E-3	.132	.0234
240	.17	112.07	.315	5.164	1.058E-2	.116	.0206
360	.25	111.738	.647	10.61	2.173E-2	.756	.1338
1176	.82	111.597	.788	12.92	2.646E-2	.047	.0084
1796	1.25	111.215	1.17	19.18	3.929E-2	.168	.0298

TABLE I-23

EVAPORATION RATE FROM LABORATORY DISH

CRUDE: TIA JUANA
EMULSIFIER: NONE
DEPTH OF FILL: FULL
VENTILATION: OPEN

DISH AREA, CM↑2 61
INITIAL SAMPLE WT, CMS: 72.438

TIME IN		WT DISH +SAMPLE	CUMULATIVE WT LOSS			RATE OF WT LOSS	
MINUTES	DAYS	GRAMS	GRAMS	MG/CM↑2	LBS/FT↑2	MICRO-GMS /CM↑2 /SEC	LBS /FT↑2 /DAY
0	0	109.121	0				
1	0	109.075	.046	.754	1.545E-3	12.57	2.224
2	0	109.042	.079	1.295	2.653E-3	9.016	1.596
3	0	109.001	.12	1.967	4.03E-3	11.2	1.983
5	0	108.942	.179	2.934	6.011E,3	8.06	1.427
6	0	108.91	.211	3.459	7.086E%S	8.743!	1.547
10	.01	108.802	.319	5.23	1.071E-2	7.377	1.306
20	.01	108.6	.521	8.541	.0175	5.519	.9768
30	.02	108.442	.679	11.13	.0228	4.317	.764
120	.08	108.185	.936	15.34	3.143E-2	.78	.1381
240	.17	107.35	1.771	29.03	5.947E-2	1.901	.3365
360	.25	107.12	2.001	32.8	.0672	.524	.0927

TABLE I-24

EVAPORATION RATE FROM LABORATORY DISH

CRUDE: TIA JUANA
EMULSIFIER: 1751
DEPTH OF FILL: FULL
VENTILATION: OPEN

DISH AREA, CM↑2 61
INITIAL SAMPLE WT, GMS: 85.086

TIME	IN	WT DISH +SAMPLE	CUMULATIVE WT LOSS			RATE OF WT LOSS	
						MICRO-GMS	LBS
MINUTES	DAYS	GRAMS	GRAMS	MG/CM↑2	LBS/FT↑2	/CM↑2 /SEC	/FT↑2 /DAY
0	0	118.89	0				
1	0	118.881	.009	.148	3.022E-4	2.459	.4352
2	0	118.875	.015	.246	5.037E-4	1.639	.29 1
3	0	118.871	.019	.311	6.38E-4	1.093	.1934
5	0	118.86	.03	.492	1.007E-3	1.503	.266
7	0	118.851	.039	.639	1.31E-3	1.23	.2176
10	.01	118.837	.053	.869	1.78E-3	1.275	.2257
20	.01	118.8	.09	1.475	3.022E-3	1.011	.1789
30	.02	118.767	.123	2.016	4.131E-3	.902	.1596
60	.04	118.691	.199	3.262	6.683E-3	.692	.1225
120	.08	118.575	.315	5.164	1.058E-2	.528	.0935
240	.17	118.365	.525	8.607	1.763E-2	.478	.0846
1090	.76	117.7	1.19	19.51	3.996E-2	.214	.0378

TABLE I-25

EVAPORATION RATE FROM LABORATORY DISH

CRUDE: TIA JUANA
EMULSIFIER: 1752
DEPTH OF FILL: FULL
VENTILATION: OPEN

DISH AREA, CM↑2 61
INITIAL SAMPLE WT, CMS: 83.304

T I M E	I N	WT DISH	CUMULATIVE WT LOSS			RATE OF WT LOSS	
MINUTES	DAYS	+SAMPLE GRAMS	GRAMS	MG/CM↑2	LBS/FT↑2	MICRO-GMS /CM↑2 /SEC	LBS /FT↑2 /DAY
0	0	111.225	0				
1	0	111.218	.007	.115	2.351E-4	1.913	.3385
2	0	111.212	.013	.213	4.366E-4	1.639	.2901
3	0	111.205	.02	.328	6.716E-4	1.913	.3385
5	0	111.196	.029	.475	9.739E-4	1.23	.2176
7	0	111.186	.039	.639	1.31E-3	1.366	.2418
10	.01	111.173	.052	.852	1.746E-3	1.184	.2095
20	.01	111.135	.09	1.475	3.022E-3	1.038	.1838
30	.02	111.101	.124	2.033	4.164E-3	.929	.1644
60	.04	111.025	.2	3.279	6.716E-3	.692	.1225
120	.08	110.907	.318	5.213	1.068E-2	.537	.0951
287	.2	110.605	.62	10.16	2.082E-2	.494	.0874
420	.29	110.321	.904	14.82	3.036E-2	.583	.1033
1440	1	109.628	1.597	26.18	5.363E-2	.186	.0329
3120	2.17	108.875	2.35	38.53	7.892E-2	.122	.0217
7200	5	107.542	3.683	60.38	.1237	.089	.0158
14500	10.07	105.312	5.913	96.93	.1986	.083	.0148
36000	25	102.602	8.623	141.4	.2896	.034	.0061

TABLE I-26

EVAPORATION RATE FROM LABORATORY DISH

CRUDE: NO.6 FUEL OIL
EMULSIFIER: 1751
DEPTH OF FILL: FULL
VENTILATION: OPEN

DISH AREA, CM↑2 61
INITIAL SAMPLE WT, CMS: 96.765

TIME IN		WT DISH +SAMPLE	CUMULATIVE WT LOSS			RATE OF WT LOSS	
MINUTES	DAYS	GRAMS	GRAMS	MG/CM↑2	LBS/FT↑2	MICRO-GMS /CM↑2 /SEC	LBS /FT↑2 /DAY
0	0	131.437	0				
1	0	131.437	0	0	0	0	0
2	0	131.436	.001	.016	3.358E-5	.273	.0484
3	0	131.435	.002	.033	6.716E-5	.273	.0484
5	0	131.432	.005	.082	1.679E-4	.41	.0725
7	0	131.429	.008	.131	2.687E-4	.41	.0725
10	.01	131.425	.012	.197	4.03E-4	.364	.0645
20	.01	131.409	.028	.459	9.403E-4	.437	.0774
30	.02	131.4	.037	.607	1.243E-3	.246	.0435
60	.04	131.364	.073	1.197	2.451E-3	.328	.058
120	.08	131.312	.125	2.049	4.198E-3	.237	.0419
240	.17	131.239	.198	3.246	6.649E-3	.166	.0294
360	.25	131.081	.356	5.836	1.196E-2	.36	.0637
2880	2	130.896	.541	8.869	1.817E-2	.02	.0036
6960	4.83	130.514	.923	15.13	.031	.026	.0045
16000	11.11	129.8	1.637	26.84	5.497E-2	.022	.0038
36000	25	129.035	2.402	39.38	8.066E-2	.01	.0018

TABLE I-27

EVAPORATION RATE FROM LABORATORY DISH

CRUDE: NO.6 FUEL OIL
EMULSIFIER: 1752
DEPTH OF FILL: FULL
VENTILATION: OPEN

DISH AREA, CM↑2 61
INITIAL SAMPLE WT, GMS: 100.11

TIME IN MINUTES	TIME IN DAYS	WT DISH +SAMPLE GRAMS	CUMULATIVE WT LOSS GRAMS	CUMULATIVE WT LOSS MG/CM↑2	CUMULATIVE WT LOSS LBS/FT↑2	RATE OF WT LOSS MICRO-GMS /CM↑2 /SEC	RATE OF WT LOSS LBS /FT↑2 /DAY
0	0	133.185	0.				
1	0	133.181	.004	.066	1.343E-4	1.093	.1934
2	0	133.181	.004	.066	1.343E-4	0	0
3	0	133.178	.007	.115	2.351E-4	.82	.1451
5	0	133.174	.011	.18	3.694E-4	.546	.0967
7	0	133.169	.016	.262	5.373E-4	.683	.1209
10	.01	133.162	.023	.377	7.724E-4	.638	.1128
20	.01	133.151	.034	.557	1.142E-3	.301	.0532
30	.02	133.145	.04	.656	1.343E-3	.164	.029
60	.04	133.115	.07	1.148	2.351E-3	.273	.0484
120	.08	133.096	.089	1.459	2.989E-3	.087	.0153
240	.17	133.062	.123	2.016	4.131E-3	.077	.0137
360	.25	133.035	.15	2.459	5.037E-3	.061	.0109
1400	.97	132.775	.41	6.721	1.377E-2	.068	.0121
1880	1.31	132.65	.535	8.77	1.797E-2	.071	.0126
7200	5	132.365	.82	13.44	2.754E-2	.015	.0026
17280	12	131.865	1.32	21.64	4.433E-2	.014	.0024

APPENDIX II

FIG. 1

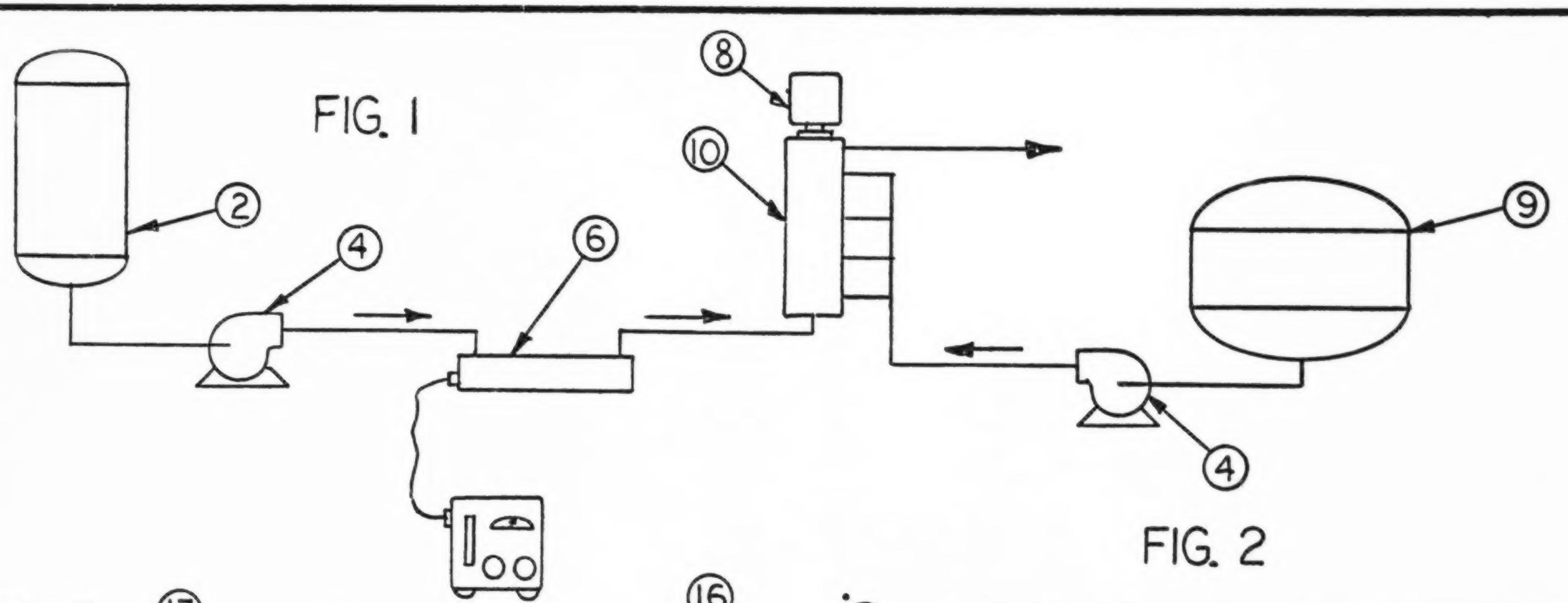


FIG. 2

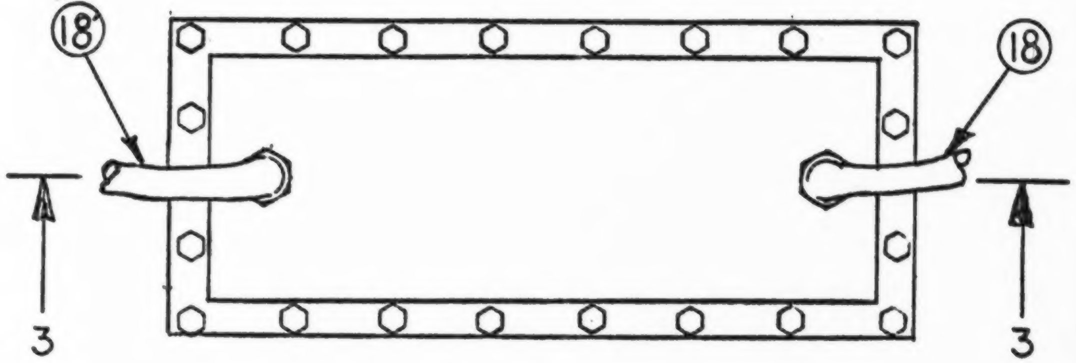


FIG. 3

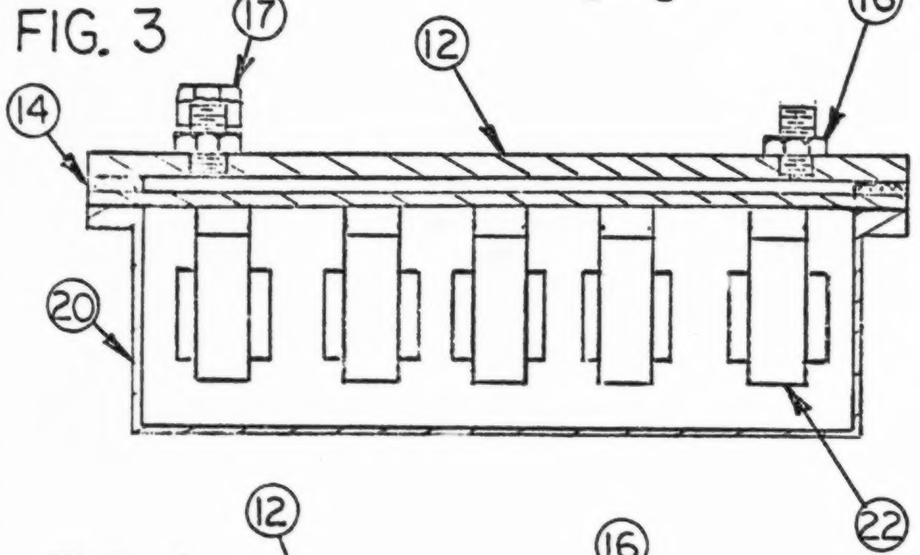
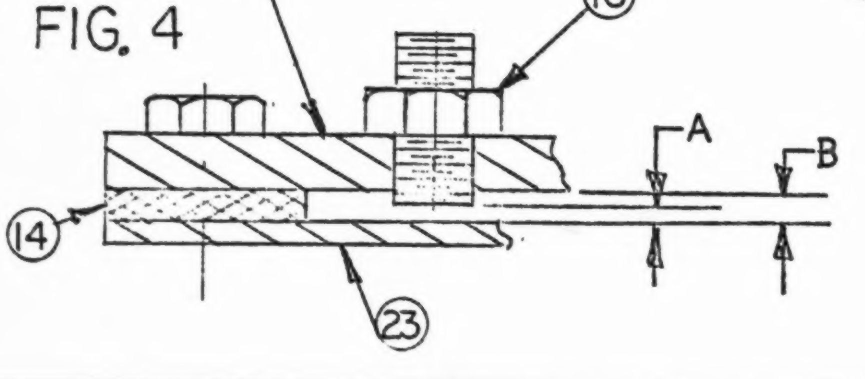

17
12
16
14
20
22

FIG. 4


12
16
A
B
14
23

SONICS INTERNATIONAL, INC.
7101 CARPENTER FREEWAY, DALLAS, TEXAS 75247

SCALE: ——	APPROVED BY:	DRAWN BY JKG
DATE: 9-9-69		REVISED ——
FLAT PLATE HOMOGENIZER DRAWINGS (DISCLOSURE)		
FIGURE II-1		DRAWING NUMBER

LEGEND

FIGURES

I. a) FIGURE 1 - Schematic of process
   b) FIGURE 2 - Top view of Item 6 in Figure 1
   c) FIGURE 3 - Cross section of Figure 2 @ 3-3

NUMBERS

II.
2) Tank or vessel (open or closed)
A) Pump
6) Ultrasonic transducer
8) Blender (or mixer motor)
9) Material being mixed or blended w/that from #2
10) Blending (or mixing) chamber
11) Ultrasonic generator
12) Face plate (steel, aluminum or plastic)
14) Gasket
16) Fitting
17) Fitting
18) Fitting
20) Transducer case
22) Transducers
23) Transducer plate

LETTERS

III. A) Distance between fitting #16 and #23 (transducer plate-this distance may be varied)

B) Distance between #12 face plate and #23 (transducer plate-this distance may also be varied).

OPERATION

A mixture of materials - properties of which prevent them from being mixed ordinarily - such as oil and water - are pumped from vessel (#2), by pump (#4), through ultrasonic transducer (#6)* which homogenizes the two (or more) liquids by irradiation with ultrasonic waves. From (#6), the liquid flows to (#10), blending (or mixing) vessel where it is mixed with material from (#9). The product of the two leaves (#10).

* This is the heart of the process. Flowing the liquid between two flat plates gives a uniform homogenization of the liquids and at a much greater quantity (or flow rate) than possible by other means available at this time.

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INPUT SECTION
CLEARINGHOUSE

As the Nation's principal conservation agency, the Department of the Interior has basic responsibilities for water, fish, wildlife, mineral, land, park, and recreational resources. Indian and Territorial affairs are other major concerns of America's "Department of Natural Resources."

The Department works to assure the wisest choice in managing all our resources so each will make its full contribution to a better United States—now and in the future.